

PROCESS FOR SELECTIVE OXIDATION OF CARBON MONOXIDE
IN A HYDROGEN CONTAINING STREAM

Field of the Invention

The invention relates to the catalytic oxidation of carbon monoxide. In
5 another of its aspects the invention relates to the selective oxidation of carbon
monoxide in the presence of hydrogen. In still another aspect the invention relates to
catalyst compositions effective in the oxidation of carbon monoxide. In yet another
aspect the invention relates to removing as much carbon monoxide as possible,
preferably all carbon monoxide, from a stream containing carbon monoxide and
10 hydrogen, particularly, to provide hydrogen feedstock for fuel cells.

Background of the Invention

The selective oxidation of carbon monoxide in hydrogen-rich streams
has been of considerable technical interest for the purification of reformed hydrogen
used in feed gas in ammonia synthesis. Recently, this selective oxidation process,
15 sometimes referred to as preferential oxidation, has attracted interest due to the
possibility of using this technology in providing suitable hydrogen fuel for fuel cells.
Since carbon monoxide is also oxidized to provide carbon dioxide for carbon dioxide
lasers, the use of catalyst which previously had been found useful in the oxidation of
carbon monoxide for use in carbon dioxide lasers has also been investigated for
20 adaptation for use in providing carbon monoxide-free hydrogen for fuel cell feedstock.

A fuel cell is an electrochemical device that enables converting the
chemical energy of fuels directly to electricity. A hydrogen-air polymer electrolyte
membrane (PEM) fuel cell stack is currently considered the best means for adapting
this technology to most uses. The PEM fuel cell is most efficient using gaseous
25 hydrogen for fuel. Use of a fuel processor to generate a hydrogen-rich feedstock at the
point of use eliminates problems of storage and distribution of the hydrogen fuel.

A fuel processor can convert fuels such as alcohol, gasoline, liquid
petroleum gas, or natural gas to a hydrogen-rich stream. By a process of steam
reforming a stream consisting primarily of hydrogen, carbon dioxide and carbon
30 monoxide can be produced, but the product is generally saturated with water.
Processing this stream in a shift reactor reduces the carbon monoxide content to

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provide relatively more hydrogen by means of the well known water-gas-shift reaction. This reaction provides a product that contains from 0.2 to 2 percent carbon monoxide by volume which is sufficient to poison the platinum-based catalyst at the PEM anode. It has now been found that, among other possibilities for removing carbon monoxide to the level necessary to prevent poisoning of the PEM catalyst, the same catalyst that is used to recombine carbon monoxide and oxygen in carbon dioxide lasers can be used to provide hydrogen feedstock for fuel cells on a level of carbon monoxide removal that is commercially viable. The operating conditions for the processes are essentially different. The removal of carbon monoxide by selective oxidation of a stream containing both carbon monoxide and hydrogen can be accomplished using the same catalyst as used in carbon dioxide lasers by controlling an increased oxygen flow to the oxidation process, raising the operating temperature of the oxidation process and avoiding reaction between oxygen and hydrogen as compared to the conditions used to recombine carbon monoxide and oxygen in carbon dioxide lasers.

Summary of the Invention

It is desirable to provide a process that is effective for catalytically oxidizing carbon monoxide with free oxygen. It is another object of this invention to provide a process for converting carbon monoxide (CO) to carbon dioxide (CO₂) in the presence of hydrogen. Again it is desirable to provide a process for producing hydrogen fuel for a fuel cell in which carbon monoxide (CO) is converted to carbon dioxide (CO₂) in the presence of hydrogen on a scale that is commercially viable.

In accordance with this invention a process is provided for the selective oxidation of carbon monoxide to carbon dioxide in a gaseous mixture comprising hydrogen and carbon monoxide. In the process an amount of free oxygen is mixed with the gaseous mixture comprising hydrogen and carbon monoxide to provide a second gaseous mixture having an enhanced oxygen to carbon monoxide mol ratio. The second gaseous mixture is contacted with a catalyst comprising platinum and iron impregnated on a support material. The carbon monoxide in the second gaseous mixture is thereby substantially completely converted to carbon dioxide. When used herein the terminology "substantially complete conversion of carbon monoxide to carbon dioxide" or similar terminology means that the amount of carbon monoxide

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present in a fuel cell feed stream is sufficiently low so as not to materially affect the functioning of a PEM catalyst.

Detailed Description of the Invention

According to this invention the process for oxidizing carbon monoxide
5 in a feed stream that also contains hydrogen can be carried out so that the CO is selectively oxidized in preference to the oxidation of the hydrogen thereby providing a means to deliver a highly pure hydrogen stream for fuel cell operation in which the oxidation of carbon monoxide in a hydrogen fuel can be integrated into a total package for generating a hydrogen-rich feedstock at the point of use.

10 The feed gas to the oxidation process can be formed in any suitable manner, such as by mixing the hydrogen that contains carbon monoxide contaminant with the O₂ containing air at any point before contact with the catalyst.

The process for oxidizing a feed containing carbon monoxide and hydrogen gas can be carried out at any pressure conditions, for any length of time, any
15 gas hourly space velocity and any volume ratio of O₂ to CO that is suitable for selective oxidation of CO in the presence of hydrogen specified in a temperature range of about 0°C to about 300°C, preferably in a range of about 25°C to about 250°C, and most preferably in a range of about 50°C to about 200°C.

The pressure during the oxidation process generally is in the range of
20 about 68.9 kPa to about 6890 kPa (about 10 psia to about 1000 psia), preferably about 96.4 kPa to about 1378 kPa (about 14 psia to about 200 psia).

The ratio of mols of O₂ in the feed gas to the mols of CO in the feed gas will generally be in the range of about 0.5 to 8.0 mol O₂/mol CO, preferably 0.5 to 4.0 mol O₂/mol CO, most preferably 0.5 to 1.5 mol O₂/mol CO.

25 The gas hourly space velocity (cc feed gas per cc catalyst per hour) can be in the range of about 100 to about 200,000, preferably from about 5,000 to about 50,000.

The hydrogen will generally be in the range of about 50-90 volume percent and the inlet CO will generally be in the range of about 0.1 to about 5 volume
30 percent.

The preparation of the catalyst useful in this invention can be carried

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out by the process disclosed in USPN 5,017,357 and USPN 4,943,550, which disclose processes using the catalyst for the recombination of carbon monoxide and oxygen for carbon dioxide lasers.

Any of the well known support materials containing metal oxide can be used as support material for the composition of matter used as catalyst in the process of this invention. Presently preferred are substantially pure alumina (aluminum oxide), titania and/or magnesium aluminate spinel. More preferably, the support material can contain at least 95 weight percent Al_2O_3 or magnesium aluminate. These materials are readily available commercially.

Generally the surface area of the support material, which can be determined by the BET/ N_2 method (ASTM D3037), is in the range of about $10 \text{ m}^2/\text{g}$ to about $350 \text{ m}^2/\text{g}$. The support can be spherical, cylindrical, trilobal, quadrilobal, ring-like or irregular in shape. Spherical support material generally has a diameter in the range of from about 0.2 mm to about 20 mm, preferably from about 1 mm to about 5 mm.

The support can also be an inert porous, ceramic material in any of the shapes cited above and coated with aluminum oxide and/or magnesium aluminate spinel.

The impregnation of the support material with platinum and iron can be carried out in any suitable manner. Generally, compounds of platinum and compounds of iron are dissolved in a suitable solvent, preferably water, to prepare a solution of suitable concentration, generally containing from about 0.005 g to about 5.0 g platinum per cc of solution and about 0.005 g to about 5.0 g iron per cc of solution. Suitable compounds of both platinum and iron are nitrates, carboxylates and acetylacetonates, among others, with acetylacetonates currently preferred. Organic solvents, such as methanol, ethanol, acetone, ethyl acetate, toluene and the like can be used as solvents for platinum or iron according to this invention. Currently, acetone is preferred.

The support material can be soaked in a solution containing platinum compounds and/or iron compounds or can be sprayed with such a solution to impregnate the support. The ratio of impregnating solution to support material is generally such that the final composition of the catalyst contains 0.05 to about 10

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weight percent platinum, preferably about 0.1 to about 5 weight percent platinum and about 0.05 to about 20 weight percent iron, preferably from about 0.1 to about 4 weight percent iron. It is in the scope of this invention to use any weight percentage of platinum and iron at which they act as copromoters of the oxidation of CO with O₂. It is presently preferred to spray a solution containing compounds of both metals onto the support, but the metal compounds can also be added separately in any order.

After impregnation the impregnated support material is heated to a temperature sufficient to drive off the solvent used in the impregnation. A flow of inert gas across the support material can be used. A temperature in the range of up to about 250°C applied for about an hour is usually sufficient for the purpose.

The dried catalyst is heat treated in an oxidizing atmosphere, preferably in an atmosphere containing free oxygen (such as air) generally at a temperature ranging from about 80°C to about 700°C for a time ranging from about 0.5 hr to about 10 hours. The heat treatment is preferably done in incremental substeps. Currently, the heat treatment is carried out at 150°C for 1 hour, 200°C for 2 hours and 400°C for 3 hours. Any combination of heating at a temperature for a time sufficient to calcine the impregnated support material to obtain at least one platinum oxide, optionally mixed with metallic platinum, and at least one iron oxide satisfies the requirements of this invention.

After the oxidation the calcined, platinum/iron impregnated support is subjected to a reduction reaction which can be carried out in any suitable manner, preferably at a temperature in the range of about 20°C to about 650°C, more preferably from about 200°C to about 500°C. Any reducing gas can be used, such as a gas containing hydrogen, CO, gaseous hydrocarbons such as methane, mixtures of the above and the like. Preferably a free hydrogen containing gas, more preferably a gas stream of substantially pure hydrogen, is employed. The reducing step can be carried out for any suitable period of time from about 1 minute to about 20 hours, preferably from about 1 hour to about 5 hours.

The reduced, platinum/iron impregnated support can be further treated by contact with any suitable organic or inorganic acid having a pH of less than about 7. Preferably, an aqueous solution of nitric acid or of a carboxylic acid (preferably acetic

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acid) is used. The previously reduced platinum/iron impregnated support is preferably soaked in about 0.01-16 mole/L of HNO_3 generally at a temperature of about 10°C to about 80°C for a period of about 0.01 to about 1 hour, but sufficiently to obtain incipient wetness.

5 After the acid treatment the impregnated support material is heated to a temperature sufficient to drive off the solvent used in the acid treatment. A flow of inert gas across the support material can be used. A temperature in the range of up to about 250°C applied for about an hour is usually sufficient for the purpose.

 The dried, acid treated catalyst is heat treated in an oxidizing
10 atmosphere, preferably in an atmosphere containing free oxygen (such as air) generally at a temperature ranging from about 80°C to about 700°C for a time ranging from about 0.5 hr to about 10 hours. The heat treatment is preferably done in incremental substeps. Currently, the heat treatment is carried out at 150°C for 1 hour, 200°C for 2 hours and 400°C for 3 hours. Any combination of heating at a temperature for a time
15 sufficient to calcine the impregnated support material to obtain at least one platinum oxide, optionally mixed with metallic platinum, and at least one iron oxide satisfies the requirements of this invention.

 Before use in the process of oxidizing carbon monoxide the oxidized, acid-treated, supported platinum/iron catalyst can be activated by a reduction step that
20 can be carried out in any suitable manner, preferably at a temperature of about 20°C to about 650°C , more preferably about 200°C to about 500°C for about 0.5 hour to about 20 hours, preferably about 1 hour to about 5 hours to enhance the activity of the catalyst composition for catalyzing a low temperature oxidation of CO with O_2 in the presence of hydrogen. Any reducing gas can be used: hydrogen, CO, paraffins and the
25 like and mixtures thereof.

 The following examples are presented in further illustration of the invention and are not to be construed as limiting the scope of the invention.

EXAMPLE I

 A catalyst precursor was prepared by weighing about 500 grams of 1/8
30 inch alumina spheres (Alcoa S-100 activated alumina) into two medium porcelain bowls and calcined at 800°C for 16 hours in a an air-purged muffle furnace. 400

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grams of the dry, calcined alumina was placed in a large porcelain bowl and- using a conventional, plastic, hand spray bottle- was sprayed with an impregnating solution prepared by dissolving 8.07 grams of platinum (II) acetylacetonate (platinum (II) 2,4 pentanedionate) and 10.13 grams of iron (III) acetylacetonate in about 650 cc of acetone. The support was stirred frequently to assure an even distribution of the solution. When about 1/4 of the impregnation solution had been applied to the support the catalyst was placed in a draft oven and heated at 175°C for 45 minutes to an hour thereby driving off the acetone and partially decomposing the metal acetylacetonates. The processes of spraying, stirring and heating were repeated three more times. When all the impregnating solution had been used the catalyst was divided equally into portions of about 202 grams each and placed in an air-purged muffle furnace heated at 150°C for 1 hour, 200°C for 2 hours and 400°C for 3 hours. This heat treatment provided two 202 gram portions of oxidized 1.0 weight percent platinum/ 0.4 weight percent iron on alumina as catalyst precursor.

EXAMPLE II

A 202 gram portion of catalyst precursor was transferred to a 2 inch diameter quartz reactor which was then mounted in a vertical tube furnace. The catalyst was activated by reducing at 300°C with about 200 cc/min hydrogen gas downflow at atmospheric pressure for three hours. The catalyst and reactor were cooled under hydrogen flow followed by nitrogen purge thereby providing an activated catalyst. This is Catalyst A.

EXAMPLE III

Another 202 gram portion of the catalyst precursor was transferred to a 2 inch diameter quartz reactor and mounted in a vertical tube furnace. The catalyst was reduced at 300°C with about 200 cc/min hydrogen gas downflow at atmospheric pressure for three hours. The catalyst and reactor were cooled under hydrogen flow followed by nitrogen purge. The freshly reduced catalyst was poured into a large bowl and impregnated in a ventilated hood with about 60 cc of concentrated nitric acid. The acid impregnation was done dropwise with stirring. The impregnation was done as quickly as possible to minimize oxidation by exposure to atmospheric oxygen. The acid treated catalyst was dried and calcined in an air-purged muffle furnace heated at

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150°C for 1 hour, 200°C for 2 hours and 400°C for 3 hours. The catalyst was transferred to a 2 inch diameter quartz reactor which was then mounted in a vertical tube furnace. The catalyst was activated by reducing at 300°C with about 200 cc/min hydrogen gas downflow at atmospheric pressure for three hours. The catalyst and
5 reactor were cooled under hydrogen flow followed by nitrogen purge thereby providing an activated, acid-treated catalyst. This is catalyst B.

EXAMPLE IV

For these conversion runs the following equipment was used. There were two separate Brooks 5850E mass flow controllers- one for the CO feed blend and
10 one for airflow. The CO blend was held in a 30-liter, aluminum, high-pressure cylinder. The CO blend normally was 1.0 percent CO with the balance being hydrogen. The air was supplied by an in house system. The CO blend and air-streams were joined at the inlet to a jacketed glass tube with an outer jacket for circulating coolant. The glass tube was cooled by a temperature controlled circulating bath which
15 could control the temperature to a specific temperature chosen from within a range of 5°C to about 100°C. The catalyst was loaded inside the glass tube.

The catalyst was prepared as set out in Examples I-III. A quantity of 2.0 grams of the treated catalyst was loaded into the glass tube with mesh quartz chips packed into the void space. Each catalyst was pretreated by heating to 97°C for one
20 hour with 100 cc/min of hydrogen flow through the catalyst bed. The tests were run with conditions as shown in the table below. All runs were carried out at ambient pressure, at 10,000 cc feed gas per cc catalyst per hour, GHSV (gas hourly space velocity) using a feed of 1 percent CO in hydrogen. Data were taken every 15 minutes with the 30 minute results recorded as the result of the test run.

TABLE 1

Pt/Fe and Pt/Fe(Acid Treated) in the Presence of Hydrogen							
Cat	React Temp °C	Target O:CO mol ratio	Actual O:CO mol ratio	%Conv O ₂	%Conv CO	CO Survival (vol%)	%Select to CO ₂
A	80	1	0.8	100.1	59.3	0.4270	75.0
A	80	2	1.6	99.9	94.9	0.0519	61.1
A	80	2.5	1.9	99.8	99.9	0.0006	51.6
A	80	2.75	2.1	99.6	100.0	0.0000	47.2
A	80	3	2.3	99.4	100.0	0.0000	43.3
B	80	1	0.8	100.0	59.5	0.4290	76.6
B	80	2	1.5	100.0	97.0	0.0314	62.7
B	80	2.5	1.9	100.0	100.0	0.0000	51.7
B	80	2.75	2.1	100.0	100.0	0.0000	47.0
B	80	3	2.3	99.9	100.0	0.0000	43.1
A	25	1	0.8	90.3	85.0	0.1570	119.2
A	25	1.5	1.2	87.6	96.5	0.0359	93.1
A	25	2	1.6	84.7	98.0	0.0202	74.4
A	25	3	2.3	80.5	98.9	0.0114	52.9
A	25	4	3.1	78.3	99.0	0.0093	41.1
B	25	1	0.8	94.6	88.7	0.1200	120.7
B	25	1.5	1.2	91.5	98.9	0.0116	91.4
B	25	1.75	1.4	88.3	99.1	0.0089	82.3
B	25	2	1.5	85.5	99.3	0.0072	75.1
B	25	2.5	1.9	82.6	99.6	0.0045	62.3
B	25	3	2.3	77.1	99.4	0.0057	55.6

In the table above cat is catalyst, react temp is reaction temperature, conv is conversion and select is selectivity.

The data show that both Pt/Fe and the Pt/Fe (acid treated) were effective as catalyst in the conversion of CO to CO₂. In oxygen conversion data the acid treated catalyst had a higher activity than the catalyst that was not acid treated.

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This higher activity occurred under all conditions, including the very high space velocities. At 80°C and 10,000 GHSV the acid treated catalyst had slightly higher CO conversion which resulted in less CO survival and a higher selectivity to CO₂. At 25°C and 10,000 GHSV the acid treated catalyst had higher CO conversion than the
5 untreated catalyst resulting in much lower CO survival and higher selectivity to CO₂.

Reasonable variations, modifications and adaptations for various conditions and uses can be made within the scope of this disclosure and the appended claims.

CLAIMS

1. A process for the selective oxidation of carbon monoxide to carbon dioxide in a gaseous mixture comprising hydrogen and carbon monoxide, which process comprises:

5 (A) mixing an amount of free oxygen with said gaseous mixture comprising hydrogen and carbon monoxide to provide an oxygen to carbon monoxide mol ratio in the range of about 0.5 to about 8.0 mol O₂/mol CO to form a second gaseous mixture;

(B) contacting the second gaseous mixture at a temperature in the range
10 of about 0°C to about 300°C with an acid treated catalyst comprising platinum and iron impregnated on a support material thereby substantially completely converting carbon monoxide in the second gaseous mixture to carbon dioxide.

2. A process according to claim 1, wherein the support material is chosen from the group consisting of alumina, magnesium aluminate and mixtures thereof.

15 3. A process according to claim 2, wherein the support material is alumina.

4. A process according to claim 1, wherein the acid treated catalyst is prepared by a process comprising:

(1) impregnating the support material with a solution comprising a
20 platinum compound and a solution comprising an iron compound thereby providing an impregnation mixture comprising an impregnated support material, platinum impregnant, iron impregnant and solvent;

(2) heating the impregnation mixture at a temperature for a time
sufficient to at least partially drive off the solvent providing thereby a dried catalyst
25 mixture;

(3) optionally, repeating steps (1) and (2) at least once;

(4) heating the dried catalyst mixture in the presence of an oxygen
containing gas at oxidizing conditions to provide an oxidized catalyst mixture;

(5) heating the oxidized catalyst mixture in the presence of a reducing
30 atmosphere at reducing conditions to provide a reduced catalyst mixture

(6) contacting the reduced catalyst mixture with an acid to provide an

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acid treated catalyst mixture and

(7) contacting the acid treated catalyst mixture with an atmosphere containing free oxygen at a temperature for a time sufficient to provide an oxidized, acid treated catalyst mixture.

5 5. A process according to claim 4, wherein the oxidized catalyst mixture is contacted with an atmosphere containing hydrogen at a temperature for a time sufficient to provide a reduced, oxidized catalyst mixture.

6. A process according to claim 5, wherein the support material is chosen from the group consisting of alumina, magnesium aluminate and mixtures thereof.

10 7. A process according to claim 6, wherein the support material is alumina.

8. A process according to claim 5, wherein the temperature at which the impregnated mixture is heated is in a range of about 125°C to about 225°C and the time at which the impregnated mixture is heated is in a range of about 0.5 hr. to about
15 1.5 hr.

9. A process according to claim 8, wherein the temperature at which the dried catalyst mixture is contacted with an atmosphere containing free oxygen is in a range of about 100°C to about 600°C and the time at which the impregnated mixture is heated is in a range of about 0.5 hr. to about 1.5 hr.

20 10. A process according to claim 4, wherein the acid used in the acid treatment is nitric acid.

11. A process according to claim 5, wherein the temperature at which the oxidized catalyst mixture is contacted with an atmosphere containing hydrogen is in the range of about 200°C to about 400°C and the time at which the oxidized catalyst
25 mixture is contacted with an atmosphere containing hydrogen is in the range of about 2 hr. to about 4 hr.

12. A process for the selective oxidation of carbon monoxide to carbon dioxide in a gaseous mixture comprising hydrogen and carbon monoxide, which process comprises:

30 (A) mixing an amount of free oxygen with said gaseous mixture comprising hydrogen and carbon monoxide to provide an oxygen to carbon monoxide

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mol ratio in the range of 0.5 to about 8.0 mol O₂/mol CO to form a second gaseous mixture;

(B) contacting the second gaseous mixture at a temperature in the range of about 0°C to about 300°C with a catalyst comprising platinum and iron

5 impregnated on a support material thereby substantially completely converting the carbon monoxide in the second gaseous mixture to carbon dioxide wherein the catalyst is prepared by a process comprising:

(1) impregnating the support material with a solution comprising a platinum compound and a solution comprising an iron compound thereby providing an

10 impregnation mixture comprising an impregnated support material, platinum impregnant, iron impregnant and solvent;

(2) heating the impregnation mixture at a temperature for a time sufficient to at least partially drive off the solvent providing thereby a dried catalyst mixture;

15 (3) optionally, repeating steps (1) and (2) at least once and

(4) heating the dried catalyst mixture in the presence of an oxygen containing gas at oxidizing conditions to provide an oxidized catalyst mixture;

(5) heating the oxidized catalyst mixture in the presence of a reducing atmosphere at reducing conditions to provide a reduced catalyst mixture

20 (6) contacting the reduced catalyst mixture with an acid to provide an acid treated catalyst mixture and

(7) contacting the acid treated catalyst mixture with an atmosphere containing free oxygen at a temperature for a time sufficient to provide an oxidized, acid treated catalyst mixture.

25 13. A process for the selective oxidation of carbon monoxide to carbon dioxide in a gaseous mixture comprising hydrogen and carbon monoxide, which process comprises:

(A) mixing an amount of free oxygen with said gaseous mixture comprising hydrogen and carbon monoxide to provide an oxygen to carbon monoxide

30 mol ratio in the range of 0.5 to about 8.0 mol O₂/mol CO to form a second gaseous mixture;

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(B) contacting the second gaseous mixture at a temperature in the range of about 0°C to about 300°C with a catalyst comprising platinum and iron impregnated on a support material thereby substantially completely converting the carbon monoxide in the second gaseous mixture to carbon dioxide wherein the catalyst
5 is prepared by a process comprising:

(1) impregnating the support material with a solution comprising a platinum compound and a solution comprising an iron compound thereby providing an impregnation mixture comprising an impregnated support material, platinum impregnant, iron impregnant and solvent;

10 (2) heating the impregnation mixture at a temperature for a time sufficient to at least partially drive off the solvent providing thereby a dried catalyst mixture;

(3) optionally, repeating steps (1) and (2) at least once and

(4) heating the dried catalyst mixture in the presence of an oxygen
15 containing gas at oxidizing conditions to provide an oxidized catalyst mixture;

(5) heating the oxidized catalyst mixture in the presence of a reducing atmosphere at reducing conditions to provide a reduced catalyst mixture;

(6) contacting the reduced catalyst mixture with an acid to provide an acid treated catalyst mixture;

20 (7) contacting the acid treated catalyst mixture with an atmosphere containing free oxygen at a temperature for a time sufficient to provide an oxidized, acid treated catalyst mixture and

(8) contacting the oxidized, acid treated catalyst mixture with an atmosphere containing hydrogen at a temperature for a time sufficient to provide a
25 reduced, oxidized, acid treated catalyst mixture.