



(51) International Patent Classification:

B01J 23/44 (2006.01) **B01J 35/10** (2006.01)
B01J 23/656 (2006.01)

(21) International Application Number:

PCT/CN2014/071883

(22) International Filing Date:

7 February 2014 (07.02.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant: **EAST CHINA UNIVERSITY OF SCIENCE AND TECHNOLOGY** [CN/CN]; No.130 Meilong Road, Xuhui District, Shanghai 200237 (CN).

(72) Inventors: **LI, Liang**; No.130 Meilong Road, Xuhui District, Shanghai 200237 (CN). **LI, Gengnan**; No.130 Meilong Road, Xuhui District, Shanghai 200237 (CN).

(74) Agent: **KING & WOOD MALLESONS**; 20th Floor, East Tower, World Financial Center, No.1 Dongsanhuan Zhonglu, Chaoyang District, Beijing 100020 (CN).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHODS, SYSTEMS AND CATALYSTS FOR OXIDIZING CARBON MONOXIDE TO CARBON DIOXIDE

(57) Abstract: Methods and catalyst compositions for oxidizing CO to CO₂ at low temperatures are disclosed. In one embodiment, a method of oxidizing CO to CO₂ may involve heating a gaseous mixture comprising at least CO and O₂ with a catalyst mixture comprising Pd disposed on a Mn₃O₄ mesoporous support at a temperature of about 0 °C to about 60 °C, and wherein the CO to CO₂ conversion rate is about 40% to about 100%.



METHODS, SYSTEMS AND CATALYSTS FOR OXIDIZING CARBON MONOXIDE TO CARBON DIOXIDE

BACKGROUND

[0001] Over the past decade, the development of catalysts to oxidize carbon monoxide (CO) at low temperatures has become an important research topic due to their wider applications in industrial and environmental fields, such as proton exchange membrane fuel cells, automobile emissions, and CO gas detection in indoor air. One important application is to control CO in gas streams for use in proton exchange membrane (PEM) fuel cells and other fuel cells. Most fuel cells suffer from the poisoning of electrodes by carbon monoxide if carbon monoxide concentration exceeds 20 ppm limit. Thus, there is a need to remove carbon monoxide from hydrogen-containing feed-gas mixture using catalysts that operate at low temperatures. Further, most CO oxidation applications involve a moist environment with rapid flow rates. Therefore, there is a need to develop moisture tolerant catalysts that can oxidize CO at low temperatures.

SUMMARY

[0002] The current disclosure provides methods to oxidize CO to CO₂ at low temperatures. In one embodiment, a method of oxidizing CO to CO₂ may involve heating a gaseous mixture comprising at least CO and O₂ with a catalyst mixture comprising at least Pd and Mn₃O₄ at a temperature of about 0 °C to about 60 °C, and wherein the CO to CO₂ conversion rate is about 40% to about 100%.

[0003] In another embodiment, a method of making a Pd/Mn₃O₄ catalyst may involve contacting Mn₃O₄ with a Pd compound to form a reaction mixture, contacting the reaction mixture with a reducing agent to form a precipitate, and isolating the precipitate.

[0004] In a further embodiment, a Pd/Mn₃O₄ catalyst comprises a mesoporous Mn₃O₄ support, and at least one Pd nanoparticle disposed on at least a portion of the mesoporous Mn₃O₄ support, wherein the Pd is present in the Pd/Mn₃O₄ catalyst in an amount of about 1 weight percent to about 5 weight percent.

5 [0005] In an additional embodiment, a system for oxidizing CO to CO₂ may include a gas source configured to supply a gaseous mixture, and a reactor configured to contain a volume of catalyst, wherein the catalyst comprises at least Pd and Mn₃O₄. The reactor further includes an inlet configured to receive the gaseous mixture such that the gaseous mixture passes through the volume of catalyst, and an outlet configured to allow gaseous mixture that has passed through the
10 volume of catalyst to exit the reactor. Further, the reactor is configured to convert CO to CO₂ at a rate of about 40% to about 100% when heated to a temperature of about 0 °C to about 60 °C.

BRIEF DESCRIPTION OF THE FIGURES

[0006] FIG. 1 depicts two possible schematics of the catalytic reactions on a surface of
15 a Pd/Mn₃O₄ catalyst according to some embodiments.

[0007] FIG. 2 illustrates catalytic activities of various catalyst mixtures according to an embodiment. FIG. 2A shows CO conversion rates of various catalytic mixtures. The x-axis is temperature in °C, and the y-axis is CO conversion in percent. The round symbols represent sample MP₀, the square symbols represent sample MP₁, the pointing up triangle symbols
20 represent sample MP₂, and the pointing down triangle symbols represent sample MP₃. FIG. 2B shows CO conversion rate of MP₂ at 5 °C (square symbols) and 60 °C (round symbols). The x-axis is time in hours, and the y-axis is CO conversion in percent.

[0008] FIG. 3A shows catalytic activity of MP2 under dry conditions (square symbols) and moist conditions (round symbols) according to an embodiment. The x-axis is temperature in °C, and the y-axis is CO conversion in percent. FIG. 3B shows stability of catalyst MP2 after prolonged reaction conditions, according to an embodiment. The x-axis is time in hours, and the y-axis is CO conversion in percent.

[0009] FIG. 4 shows X-ray diffraction pattern of Pd/Mn₃O₄ catalysts according to an embodiment; (a) is MP0, (b) is MP1, (c) is MP2, and (d) is MP3. The x-axis is 2 Θ (Cu K Θ), and the y-axis is intensity.

[0010] FIG. 5 shows TEM images of Pd/Mn₃O₄ catalysts. Inset shows the corresponding SAED patterns. (A) TEM image of MP0; (B) energy diffraction spectra of MP0 (the x-axis is energy (KeV), and the y-axis is intensity (a.u.)); (C) TEM image of MP1; (D) HRTEM image of MP1; (E) TEM image of MP2; (F) HRTEM image of MP2; (G) TEM image of MP3; and (H) HRTEM image of MP3.

[0011] FIG. 6 shows N₂ adsorption-desorption isotherms of Pd/Mn₃O₄ catalysts before and after the reaction according to an embodiment. Insets show corresponding pore size distributions. (A) is MP0, (B) is MP1, (C) is MP2, and (D) is MP3. The x-axis is relative pressure (P/P₀), and the y-axis is volume absorbed (cm³/g STP). The graph insets show the pore size in nm.

[0012] FIG. 7 shows XPS spectra of Pd/Mn₃O₄ catalysts before (A, B, C) and after (D, E, F) the reaction according to an embodiment. (a) MP0; (b) MP1; (c) MP2; (d) MP3; (e) fresh MP2 catalyst; (f) MP2 catalyst after CO oxidation under normal conditions; and (g) MP2 catalyst after CO oxidation under moist conditions. The x-axis is binding energy (eV), and the y-axis is intensity.

[0013] FIG. 8 shows H₂-TPR profiles of Pd/Mn₃O₄ catalysts according to an embodiment. (a) MP0; (b) MP1; (c) MP2; (d) MP3. The x-axis is temperature (°C), and the y-axis is intensity (a.u.).

5 DETAILED DESCRIPTION

[0014] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

[0015] The present disclosure provides catalyst compositions and methods to oxidize
10 CO to CO₂ at low temperatures. The catalyst employed is a Pd catalyst supported on a mesoporous Mn₃O₄ support. The mesoporous Mn₃O₄ support disclosed herein are economical to manufacture, with simple processes. Further, Mn₃O₄ has high mechanical strength and abrasion resistance at any temperature at which it serves for CO oxidation.

[0016] In some embodiments, the mesoporous Mn₃O₄ support may be produced by
15 mixing a triblock copolymer, a manganese salt, and a solvent to form a solution, heating the solution to form a product, and calcining the product. Non-limiting examples of manganese salt include Mn(NO₃)₂, MnCl₂, MnBr₂, MnF₂, MnPO₄, MnSO₄, or any combination thereof. Examples of triblock polymers that may be used include, but are not limited to, poly(ethyleneglycol)-poly(propyleneglycol)-poly(ethyleneglycol), poly(ethyleneimine)-
20 poly(ethyleneglycol)-poly(ethyleneimine), poly(ethyleneglycol)-polyacetal-poly(ethyleneglycol), polyacetal-poly(ethyleneglycol)-polyacetal, or any combinations thereof.

[0017] In some embodiments, the manganese salt and the triblock polymer are mixed with a solvent, such as ethanol, propanol, ether, acetone, ethyl acetate, water, dimethyl-

formamide, or any combination thereof. Mixing may be performed by any method known in the art. Suitable time periods for this mixing process may include from about 30 minutes to about 2 hours, about 30 minutes to about 1.5 hours, about 30 minutes to about 1 hour, or about 30 minutes to about 45 minutes. Specific examples include about 30 minutes, about 45 minutes, 5 about 1 hour, about 1.25 hours, about 1.5 hours, about 2 hours, and ranges between any two of these values (including their endpoints). In some cases, longer periods of times may be used.

After the mixing step, the solution is evaporated. This step may be performed by any known process in the art, such as heating, rotary evaporation, air drying, or evaporating in an oven until the solution is substantially evaporated. For example, the solution may be heated to about 50 °C

10 to about 80 °C, about 50 °C to about 70 °C, about 50 °C to about 60 °C, or about 50 °C to about 55 °C. Specific examples include about 50 °C, about 55°C, about 60 °C, about 70 °C, about 80 °C, and ranges between any two of these values. Suitable time periods for this evaporation step may include about 24 hours to about 96 hours, about 24 hours to about 72 hours, about 24 hours to about 48 hours, or about 24 hours to about 36 hours. Specific examples include about 24 hours, 15 about 48 hours, about 60 hours, about 72 hours, about 96 hours, and ranges between any two of these values (including their endpoints). The product obtained by these processes may be a xerogel.

[0018] In some embodiments, the product obtained after solvent evaporation is further calcined generally at about 300 °C to about 600 °C, for about 30 minutes to about 6 hours, about 20 30 minutes to about 5 hours, about 30 minutes to about 3 hour, or about 30 minutes to about 2 minutes. Specific examples include about 30 minutes, about 45 minutes, about 2 hour, about 4 hours, about 5 hours, about 6 hours, and ranges between any two of these values (including their endpoints). Calcination refers to a process of heating a substance to a high temperature but below

the melting or fusing point, and may cause loss of moisture, reduction and/or oxidation. This process may be performed by any known methods in the art, such as using furnaces, rotary kilns, fluidized bed reactors, and the like. The shape and the size of the Mn_3O_4 mesoporous support thus produced are not specifically defined. The support may have any desired shape and structure, for example, the support may be in any form of powders, spheres, granules, honeycombs, and the like, or combinations thereof.

[0019] For applying palladium to the mesoporous support, the steps may include contacting the Mn_3O_4 mesoporous support, with a palladium compound to form a reaction mixture, contacting the reaction mixture with a reducing agent to form a precipitate, and isolating the precipitate. Non-limiting examples of palladium compound include Na_2PdCl_4 , H_2PdCl_4 , K_2PdCl_4 , $(\text{NH}_4)_2\text{PdCl}_4$, $\text{Pd}(\text{CH}_3\text{COO})_2$, $\text{Pd}(\text{NO}_3)_2$, PdSO_4 , or any combination thereof. The palladium solution may be applied to the Mn_3O_4 mesoporous support in any ordinary method of mixing, dipping, co-precipitation, or competitive adsorption. The conditions for the treatment may be suitably selected, depending on the method employed. In some embodiments, the Mn_3O_4 mesoporous support is mixed with the Pd compound for about 1 hour to about 3 hours, about 1 hour to about 2 hours, or about 1 hour to about 1.5 hours. Specific examples include about 1 hour, about 1.25 hours, about 1.5 hours, about 2 hours, about 3 hours, and ranges between any two of these values (including their endpoints). In some embodiments, the Mn_3O_4 mesoporous support may be kept in contact with the palladium solution at a temperature between room temperature and 90°C , for about 1 minute to about 10 hours.

[0020] In some embodiments, a reducing agent may be added to the above described Mn_3O_4 -Pd reaction mixture to precipitate the Pd/ Mn_3O_4 catalyst. Suitable reducing agents that may be used are hydrazine, NaBH_4 , KBH_4 , or any combination thereof. Suitable time periods for

mixing this reducing agent and Mn_3O_4 -Pd mixture may be about 8 hours to about 24 hours, about 8 hours to about 20 hours, about 8 hours to about 16 hours, or about 8 hours to about 12 hours.

Specific examples include about 8 hours, about 12 hours, about 16 hours, about 20 hours, about 24 hours, and ranges between any two of these values (including their endpoints). The precipitate

5 obtained may be isolated by any known process in the art, such as centrifugation, filtration, distillation, decantation, or any combination thereof. The precipitate is further washed and dried by rotary evaporation or air drying, or by any other similar process.

[0021] Disclosed herein are catalyst compositions that may be used for oxidizing CO to CO_2 . In some embodiments, a Pd/ Mn_3O_4 catalyst made by the steps described herein may

10 comprise a mesoporous Mn_3O_4 support, and at least one Pd nanoparticle disposed on at least a portion of the mesoporous Mn_3O_4 support, wherein the Pd is present in the Pd/ Mn_3O_4 catalyst in an amount of about 1 weight percent to about 5 weight percent. In some embodiments, the amount of Pd nanoparticle in the catalyst may be in the range of about 1 weight percent to about 5 weight percent, about 1 weight percent to about 4 weight percent, about 1 weight percent to
15 about 3 weight percent, or about 1 weight percent to about 2 weight percent of the catalyst.

Specific examples include about 1 weight percent, about 1.5 weight percent, about 2.5 weight percent, about 3 weight percent, about 4 weight percent, about 5 weight percent, and ranges between any two of these values (including their endpoints).

[0022] In some embodiments, the Mn_3O_4 mesoporous support may have a disordered or
20 ordered pore structure. In some embodiments, Mn_3O_4 mesoporous support has an average pore diameter of about 1 nanometer to about 50 nanometers, about 1 nanometer to about 40 nanometers, about 1 nanometer to about 25 nanometers, or about 1 nanometer to about 10 nanometers. Specific examples include about 1 nanometer, about 5 nanometers, about 15

nanometers, about 25 nanometers, about 50 nanometers, and ranges between any two of these values (including their endpoints).

[0023] In some embodiments, the Mn_3O_4 mesoporous support has an average pore volume of about $0.2 \text{ cm}^3/\text{gram}$ to about $1 \text{ cm}^3/\text{gram}$, about $0.2 \text{ cm}^3/\text{gram}$ to about $0.8 \text{ cm}^3/\text{gram}$,
5 about $0.2 \text{ cm}^3/\text{gram}$ to about $0.6 \text{ cm}^3/\text{gram}$, about $0.2 \text{ cm}^3/\text{gram}$ to about $0.5 \text{ cm}^3/\text{gram}$, or about $0.2 \text{ cm}^3/\text{gram}$ to about $0.3 \text{ cm}^3/\text{gram}$. Specific examples include about $0.2 \text{ cm}^3/\text{gram}$, about $0.4 \text{ cm}^3/\text{gram}$, about $0.6 \text{ cm}^3/\text{gram}$, about $0.8 \text{ cm}^3/\text{gram}$, about $1 \text{ cm}^3/\text{gram}$, and ranges between any two of these values (including their endpoints).

[0024] In some embodiments, the Mn_3O_4 mesoporous support has an average BET
10 (Brunauer-Emmett-Teller) surface area of about $60 \text{ m}^2/\text{gram}$ to about $150 \text{ m}^2/\text{gram}$, about $60 \text{ m}^2/\text{gram}$ to about $120 \text{ m}^2/\text{gram}$, about $60 \text{ m}^2/\text{gram}$ to about $100 \text{ m}^2/\text{gram}$, or about $60 \text{ m}^2/\text{gram}$ to about $75 \text{ m}^2/\text{gram}$. Specific examples include about $60 \text{ m}^2/\text{gram}$, about $80 \text{ m}^2/\text{gram}$, about $100 \text{ m}^2/\text{gram}$, about $150 \text{ m}^2/\text{gram}$, and ranges between any two of these values (including their endpoints).

15 [0025] In some embodiments, the Pd nanoparticles may be disposed on the surface or in a pore channel of the mesoporous Mn_3O_4 support, or any combination thereof. In some embodiments, Pd nanoparticles may be uniformly arranged on and/or throughout the support. In some embodiments, the concentration of the Pd nanoparticle disposed or located on the inner surface of the mesoporous Mn_3O_4 support is greater than a concentration of the catalyst disposed
20 on the outer surface of the support. In other words, more Pd nanoparticles may be disposed or located within the pores of the support, as compared to the outer surface of the support.

[0026] Disclosed herein are methods to convert carbon monoxide (CO) to carbon dioxide (CO_2) at low temperatures. In some embodiments, a method of oxidizing CO to CO_2

may involve heating a gaseous mixture comprising at least CO and O₂ with a catalyst mixture comprising at least Pd and Mn₃O₄ at a temperature of about 0 °C to about 60 °C, and wherein the CO to CO₂ conversion rate is about 40% to about 100%. The Pd/Mn₃O₄ catalyst mixture include Pd nanoparticles disposed on the surface and/or in a pore channel of the mesoporous Mn₃O₄

5 support, as described herein. In some embodiments, the gaseous mixture may also include N₂, He, H₂, Ar, or any combination thereof. Additionally, the gaseous mixture may also contain water, water vapor, moisture, or any combination thereof.

[0027] In some embodiments, the CO may be present in the gaseous mixture in an amount of about 1 volume percent to about 10 volume percent, about 1 volume percent to about 8 volume percent, about 1 volume percent to about 6 volume percent, or about 1 volume percent to about 4 volume percent of the gaseous mixture. Specific examples include about 1 volume percent, about 2 volume percent, about 4 volume percent, about 6 volume percent, about 8 volume percent, about 10 volume percent, and ranges between any two of these values (including their endpoints).

15 [0028] The catalysts disclosed herein can function at temperatures at or below 60 °C, and can convert CO to CO₂ efficiently. In some embodiments, the gaseous mixture may be heated to a temperature of about 20 °C to about 30 °C, about 20 °C to about 26 °C, about 20 °C to about 25 °C, or about 20 °C to about 22 °C. Specific examples include about 20 °C, about 22 °C, about 25 °C, about 27 °C, about 30 °C, and ranges between any two of these values (including their endpoints). When performed at these temperatures, conversion rate of the CO to CO₂ is about 60 % to about 100 %, about 60 % to about 90 %, or about 60 % to about 75 %. In some embodiments, the conversion rate of the CO to CO₂ is at least 60 %, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%., at least 99%, or 100%.

20

[0029] In some embodiments, the gaseous mixture may be heated to a temperature of about 30 °C to about 60 °C, about 30 °C to about 50 °C, about 30 °C to about 40 °C, or about 30 °C to about 35 °C. Specific examples include about 30 °C, about 35 °C, about 45 °C, about 50 °C, about 60 °C, and ranges between any two of these values (including their endpoints). When performed at these temperatures, conversion rate of the CO to CO₂ is about 60 % to about 100 %, about 60 % to about 90 %, or about 60 % to about 75 %. In some embodiments, the conversion rate of the CO to CO₂ is at least 60 %, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, at least 99%, or 100%.

[0030] In some embodiments, the gaseous mixture may be heated to a temperature of about 0 °C to about 10 °C, about 0 °C to about 5 °C, about 0 °C to about 3 °C, or about 0 °C to about 2 °C. Specific examples include about 0 °C, about 3 °C, about 4 °C, about 5 °C, about 10 °C, and ranges between any two of these values (including their endpoints). When performed at these temperatures, conversion rate of the CO to CO₂ is about 40 % to about 60 %, about 40 % to about 50 %, or about 40 % to about 45 %. In some embodiments, the conversion rate of the CO to CO₂ is at least 40 %, at least 45%, at least 50%, at least 55%, or at least 60%.

[0031] In some embodiments, the gaseous mixture may be heated to a temperature of about 0 °C to about 60 °C, about 0 °C to about 50 °C, about 0 °C to about 30 °C, or about 0 °C to about 15 °C. Specific examples include about 0 °C, about 5 °C, about 25 °C, about 30 °C, about 60 °C, and ranges between any two of these values (including their endpoints). When performed at these temperatures, conversion rate of the CO to CO₂ is about 40 % to about 100 %, about 40 % to about 90 %, about 40 % to about 85 %, about 40 % to about 75 %, or about 40 % to about 50 %. In some embodiments, the conversion rate of the CO to CO₂ is at least 40 %, at least

50%, at least 60%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, at least 99%, or 100%.

[0032] In some embodiments, the process of CO to CO₂ conversion may also be performed in the presence of water, water vapor, or moisture. In some embodiments, the Pd/Mn₃O₄ catalyst mixture described herein may catalyze the CO oxidation more efficiently in the presence of a water molecule. Without wishing to be bound by theory, the Pd may oxidize CO to CO⁺ species, which then may react with OH[⊖] to form a reactive intermediate COOH. COOH may decompose to CO₂ and H[•]. Further, the O[⊖] species generated by Mn₃O₄ support may combine with H[•] and H⁺ to form H₂O (FIG. 1). Thus, it is possible that CO₂ formation occurs only on the surface of palladium, without contacting Mn₃O₄, and preventing the formation of carbonates. Therefore, even in the presence of water, the catalytic activity is not diminished and CO oxidation proceeds.

[0033] The CO oxidation process described herein may be performed as a batch process or a continuous flow process. In the batch process, the gaseous mixture comprising CO and O₂ is filled in the reactor at the beginning of the reaction period, after which the reactor is closed for the entire period without adding additional components. In the continuous flow process, the reactor may be filled continuously with fresh gaseous mixture and also emptied continuously. The reactor vessel may be configured to receive the gaseous mixture, the catalyst mixture, or any other reactants separately or in any combination. In a continuous flow process, the gaseous mixture can be in contact with the Pd/Mn₃O₄ catalyst mixture at a flow rate of about 40 mL per minute to about 60 mL per minute, about 40 mL per minute to about 50 mL per minute, or about 40 mL per minute to about 45 mL per minute. Further, the flow rate may also depend on the size

of the reactor and the volume of the catalyst used. Larger reactors may allow higher flow rates, and smaller reactors may allow smaller flow rates.

[0034] An exemplary continuous flow system may comprise the following: a gas source configured to supply a gaseous mixture, and a reactor configured to contain a volume of catalyst, wherein the catalyst comprises mesoporous Pd/Mn₃O₄ as described herein. The reactor may comprise an inlet configured to receive the gaseous mixture such that the gaseous mixture passes through the volume of catalyst, and an outlet configured to allow gaseous mixture that has passed through the volume of catalyst to exit the reactor. Further, the reactor is configured to convert CO to CO₂ at a rate of about 40% to about 100% when heated to a temperature of about 0 °C to about 60 °C. The reactor may be further connected to a thermoelectric couple, a pressure gauge, a temperature controller, a cooling system, a mechanical stirrer, a plurality of gas valves, or any combination thereof.

[0035] The process and the catalysts disclosed herein may be used to remove carbon monoxide from hydrogen-rich gas used for fuel cells, to prevent carbon monoxide poisoning of electrodes. Further, these methods can also be applied for other areas where low-temperature carbon monoxide elimination is required, such as automotive applications, air cleaning systems, for example, carbon monoxide removal at ambient temperatures in tunnels, metro, parking areas, garages, submarines, and also in respiratory protection systems. It can be used for removal of CO in chemical plants, power generation plants, ammonia plants, and during polymerization reactions of hydrocarbons.

EXAMPLES

EXAMPLE 1: Synthesis of mesoporous Mn₃O₄

[0036] About 1.0 gram of poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (P-123) and 0.01 mole of Mn(NO₃)₂ were added to 10 mL of anhydrous ethanol and vigorously stirred for 60 minutes. The mixture was transferred to an oven and the solvent was evaporated at 60 °C for 48 hours. The resulting xerogel was calcined at 500 °C for 1 hour to remove the P-123 PEG template.

EXAMPLE 2: Synthesis of Pd/Mn₃O₄ catalyst

[0037] A series of mesoporous Mn₃O₄ supported Pd catalysts were synthesized through impregnation and reduction procedures. In a typical synthesis, about 0.5 gram mesoporous Mn₃O₄ material of Example 1 was added to 25 mL Na₂PdCl₄ solution (at concentrations ranging from 0.1×10^{-4} - 0.5×10^{-4} mM) and stirred for 2 hours. About 100 mL of 0.1 M hydrazine hydrate (NH₂NH₂·H₂O) was added and stirred for 12 hours to obtain a precipitate. The resulting solid mass was collected through centrifugation, washed with water and dried at 60 °C for 24 hours. Examples of catalyst mixtures with various Pd loadings and their physiochemical properties are shown in Table 1.

TABLE 1

sample	Pd loadings(wt. %)	BET surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
MP0	-	73	4.3	0.34
MP1	1.1	84	3.3	0.33
MP2	2.7	130	2.6	0.33
MP3	3.2	97	2.0	0.24

EXAMPLE 3: CO oxidation

[0038] The catalytic test for CO oxidation was carried out in a fixed-bed quartz tubular reactor (6 mm) containing 200 milligrams of catalyst samples of Table 1 without any pretreatment. A standard gaseous mixture containing 1.0 vol% CO, 20.0 vol% O₂ and 79.0 vol% N₂ was used as a source. The feed gas at a flow rate of 50 mL min⁻¹ was introduced into the reactor using mass-flow controllers, corresponding to a space velocity of 15000 mL h⁻¹ g⁻¹_{cat}. After a steady flow of gas for 10 minutes, the activity of catalyst was tested. The conversion of CO was measured by online gas chromatograph (GC) equipped with a flame ionization detector (FID) under steady-state conditions. The reaction temperature was monitored by a thermocouple placed in the middle of the catalyst bed. Conversion of CO was calculated as follows:

$$\text{Conversion (\%)} = (\text{Moles of reactant converted} / \text{Moles of reactant in feed}) \times 100\%$$

[0039] The catalytic performances of various Pd/Mn₃O₄ catalysts are shown in FIG. 2A, where the CO conversion is reported as a function of temperature. The mesoporous Mn₃O₄ support alone did not show any obvious catalytic activity at any temperature. After incorporation of palladium on the mesoporous support, the catalytic activity increased greatly. Further, increase in the Pd loading content from 1.1 % to 2.7 % decreased the T₁₀₀ temperature (temperature at which CO conversion is 100%) from 30 °C to 25 °C. Further increase in Pd content to 3.2% did not produce any sequential decrease of the conversion temperature. To measure the intrinsic activity of the catalysts, the turnover frequencies (TOFs) based on surface palladium atoms were also calculated. Compared to other MnO_x supported Pd catalysts, such as Pd/Mn₂O₃ and Pd/MnO₂, all the samples showed relatively high TOFs at 20 °C, and exhibited excellent catalytic activity. The 2.7% Pd loaded Mn₃O₄ sample (MP2) gave a TOF value of

0.0637 s⁻¹, exhibiting significantly higher catalytic activity than that of 1.1% Pd loaded (MP1, 0.0109 s⁻¹) and 3.2% Pd loaded sample (MP3, 0.0534 s⁻¹). The turnover frequencies (TOFs) were calculated at 20 °C based on the following definition: TOF (s⁻¹) = moles of reactant converted / (moles of total active sites × reaction time).

5 **[0040]** The 2.7% Pd loaded catalyst (MP2) was further tested at different temperatures for its ability to convert CO to CO₂. As shown in FIG. 2B, the T₁₀₀ temperature was about 22 °C and T₅₀ temperature (temperature at which CO conversion is 50%) was around 0 °C. The catalytic activity of MP2 did not decrease even after 30 hours of reaction.

10 EXAMPLE 4: CO oxidation under moist conditions

[0041] The catalytic activity (MP2) in the presence of moisture condition was tested as in Example 3 by passing the feed gas of 1% CO at a flow rate of 50 mL min⁻¹ through a water vapor saturator directly introduced into the catalyst bed. The water concentration in the feed gas was about 4% by volume. As shown in FIG. 3A, the T₁₀₀ temperature decreased from 25 °C
15 (under dry conditions) to 22 °C (under moist conditions), and the T₅₀ temperature was lower than 0 °C. Further, there was no change in the catalytic activity of MP2 even after 30 hours, as indicated in FIG. 3B. These studies showed that mesoporous Pd/Mn₃O₄ catalyst performed much better under moist conditions when compared to dry conditions.

20 EXAMPLE 5: Characterization of mesoporous Pd/Mn₃O₄ catalysts

[0042] Various Pd/Mn₃O₄ catalysts were prepared as in Example 2. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus powder diffractometer (Billerica, MA, USA) with graphite monochromatized Cu Kα radiation (λ=0.15405 nm) operated at 40 kV.

Nitrogen adsorption and desorption isotherms were measured on a Micromeritics ASAP 2020 M analyzer (Norcross, GA, USA) at liquid nitrogen temperature (77 K). Prior to the measurements, the samples were degassed at 523K in vacuum for 6 hours. The specific surface area and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

[0043] The crystalline structures of MP0, MP1, MP2, and MP3 were first characterized by X-ray diffraction (XRD) analysis. FIG. 4 depicts the XRD pattern obtained of the various catalysts. There were no diffraction peaks in the small angle range indicating the disordered pore arrangement. However, a series of sharp and symmetrical Bragg diffraction peaks were observed in the wide angle area, which demonstrated the crystalline feature. All the peaks in the pattern were assigned to the characteristic reflection planes of tetragonal Mn_3O_4 . No additional peaks relating to impurity were found. Besides, the lattice constants, $a = 5.753 \text{ \AA}$ and $c = 9.436 \text{ \AA}$, were also in agreement with those of bulk Mn_3O_4 (PDF card no. 80-0382). When loaded with Pd, a peak emerged at $2\theta = 40^\circ$ which could be identified as (111) diffraction bands of face-centered cubic structure palladium (PDF card no. 65-6174). The diffraction intensity increased correspondingly with the increase in loaded Pd content. It should be noted that all the characteristic peaks of metallic Pd were broad and weak, indicating the highly dispersed amorphous or small palladium.

[0044] Transmission electron microscopy (TEM) observations were performed on a field emission JEM-2100 (JEOL) electron microscope operated at 300kV and equipped with a Gatan-666 electron energy loss spectrometer and energy dispersive X-ray spectrometer. FIG. 5 shows the TEM results of meso-structured Mn_3O_4 support and its Pd loading catalysts. All the samples had a porous structure with a pore network inter-sectioned by nanocrystals, and no

obvious differences were found between the samples. For Pd loaded catalysts, there were no Pd particles in the image even at 3.2 wt% loadings, suggesting that Pd particles were highly dispersed. The Selected-area-electron diffraction (SAED) patterns from the same area were also imaged. The well-defined diffraction rings for Mn_3O_4 were observed in all the samples. However, metallic Pd (111) diffraction ring only emerged when Pd loading content was higher than 2.7 wt%. The relatively faint on-again/off-again properties indicated its much lower crystallinity, and agreed with the above XRD results. Further, the High Resolution Transmission Electron microscopy (HRTEM) investigation clearly showed that the catalysts were composed of crystal Mn_3O_4 and Pd nanoparticles (FIG.5 D, F, H). Nanocrystals with different lattice d-spacing were found all over the image. The d-spacing of Pd crystal was found to be 2.2 Å, and other d-spacing values presented in the images belong to Mn_3O_4 nanoparticles. The average diameter of Mn_3O_4 collected from over 10 different particles was 18 nm. Further, the highly dispersed Pd crystals on the Mn_3O_4 support had an average diameter of lower than 10 nm.

[0045] The porous structure of the samples were further investigated by measuring adsorption-desorption isotherms of nitrogen at 77 K, as shown in FIG. 6. The pore structure parameters are summarized in Table 1. In all the cases, the typical Langmuir IV isotherms with H3 hysteresis loops were observed and indicated their porous structure and the formation of slit-like mesopores. The mesoporous structure of the Mn_3O_4 support did not change significantly after impregnation and reduction treatment. However, their specific surface areas increased after loading with palladium. This may be due to the opening of some of the pore channels in the meso-structured Mn_3O_4 support, when treated with acidic solution of NaPdCl_4 during the impregnation and reduction treatment. However, the pore size and pore volume of the Pd/ Mn_3O_4 samples did not change with the increased Pd loading. These results demonstrated that palladium

nanoparticles were highly dispersed both inside the pore channels and on the surface of the support.

[0046] X-ray photoelectron spectroscopy analysis (XPS) was used to determine surface chemical states of the species for meso-structured Mn_3O_4 and its Pd loading catalysts. XPS (X-ray photoelectron spectroscopy) signals were collected on a VG Micro MK operated at 200 W. All the elemental binding energies were referenced to the C (1s) line situated at 284.6 eV. As shown in FIG. 7, all the samples exhibited two binding energy levels, at Mn 2p_{3/2} (642.4 eV) and Mn 2p_{1/2} (654.0 eV) (Fig. 4A). The resolution of Mn 2p_{3/2} produced three characteristic peaks at about 640.2 eV, 641.5 eV and 643.5 eV, corresponding to Mn^{2+} , Mn^{3+} , and Mn^{4+} respectively. The calculated content of different manganese species clearly indicated that the surface manganese were mainly Mn^{3+} and Mn^{4+} , and the Mn^{2+} species only occupied about 1%. This may be due to the partial oxidation of surface manganese species when exposed to air. The O 1s spectra recorded from these support and catalysts are also shown in FIG. 7B. The distribution of oxygen species were estimated by de-convolution, and are depicted in the figure. Two kinds of oxygen species were observed, one at 530.4 eV which is typical of metal-oxygen bonding, and the other at 531.5 eV and 532.3 eV, which are usually associated with the surface adsorbed oxygen. With the increase in Pd loading amount, the lattice O decreased. This may be attributed to the highly dispersed Pd nanoparticles on the Mn_3O_4 surface. Further, the palladium element showed the typical Pd0 adsorptions at 335.0 and 340.3 eV, corresponding to 3d_{5/2} and 3d_{3/2}, respectively, with a spin-orbit separation of 4.7 eV. The three Pd/ Mn_3O_4 samples displayed 3d_{5/2} and 3d_{3/2} absorption peaks that were slightly higher than that of Pd0. After curve fitting, the calculated content of Pd0 and Pd^{2+} were about 90% and 10%, respectively. These data

clearly confirms that most of the Pd^{2+} ions on the surface are reduced to Pd0 by hydrazine hydrate.

[0047] H_2 -Temperature-Programed Reduction (H_2 -TPR) experiments were carried out to investigate the redox properties of various Mn_3O_4 supported palladium catalysts. H_2 temperature-programmed reduction (H_2 -TPR) analysis was performed by using a Micromeritics Chemisorb 2750 apparatus. For each analysis, accurate amounts of calcined sample (50 milligrams) were purged in a flow of pure argon at 200 °C for 30 minutes to remove traces water (heating rate 10 °C/minute). After cooling to room temperature, H_2 -TPR experiments were performed using a 10 vol% H_2/Ar mixture at a flow rate of 25 mL/minute. The sample was heated from ambient temperature to 700 °C at heating rate of 10 °C/min and H_2 consumption was detected by a thermal conductivity detector (TCD). FIG. 8 shows the reduction profiles of the catalysts. For comparison, the TPR profile of the parent Mn_3O_4 was also included. It is well documented that the manganese oxides are reduced between 300 °C and 600 °C. The meso-structured Mn_3O_4 support exhibited two reduction peaks, one at 330 °C and the other at 510 °C, indicating the stepwise reduction of manganese. Without wishing to be bound by theory, the lower temperature peak may be attributed to the reduction of Mn^{4+} to Mn^{3+} , whereas the higher one can be due to the consecutive reduction of Mn^{3+} to Mn^{2+} . These results further corroborate the above XPS analysis. When palladium was incorporated, two reduction peaks shifted to lower temperatures. This shift is due to the presence of spillover effect involving either hydrogen activated on the metal phase or mobile lattice oxygen induced by intimate metal-support interactions. The significant low-temperature reduction feature strongly suggests that the manganese oxide is 'activated' to a large extent in the Pd/ Mn_3O_4 catalyst.

[0048] In the above detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be used, and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

[0049] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0050] As used in this document, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical

and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term “comprising” means “including, but not limited to.”

[0051] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0052] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0053] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (*e.g.*, bodies of the appended claims) are generally intended as “open” terms (*e.g.*, the term “including” should be interpreted as “including but not limited to,” the term “having” should be interpreted as “having at least,” the term “includes” should be interpreted as “includes but is not limited to,” etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases “at least one” and “one or more” to introduce claim

recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and
5 indefinite articles such as "a" or "an" (*e.g.*, "a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (*e.g.*, the bare recitation of "two recitations," without other
10 modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (*e.g.*, "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C
15 together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (*e.g.*, "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will
20 be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms,

or both terms. For example, the phrase “A or B” will be understood to include the possibilities of “A” or “B” or “A and B.”

[0054] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby

5 described in terms of any individual member or subgroup of members of the Markush group.

[0055] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at

10 least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc.

As will also be understood by one skilled in the art all language such as “up to,” “at least,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a

15 range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0056] Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently

20 unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

WHAT IS CLAIMED IS:

1. A method of oxidizing CO to CO₂, the method comprising:
heating a gaseous mixture comprising at least CO and O₂ with a catalyst mixture
comprising at least Pd and Mn₃O₄ at a temperature of about 0 °C to about 60 °C;
5 wherein the CO to CO₂ conversion rate is about 40% to about 100%.
2. The method of claim 1, wherein the catalyst mixture comprises at least one Pd
nanoparticle disposed on at least a portion of a Mn₃O₄ support.
- 10 3. The method of claim 1, wherein the gaseous mixture is heated to a temperature of about
20 °C to about 30 °C, and a conversion rate of the CO to CO₂ is about 90 % to about
100 %.
4. The method of claim 1, wherein the gaseous mixture is heated to a temperature of about
15 20 °C to about 30 °C, and a conversion rate of the CO to CO₂ is at least about 80 %.
5. The method of claim 1, wherein the gaseous mixture is heated to a temperature of about 0
°C to about 10 °C, and a conversion rate of the CO to CO₂ is about 40 % to about 50 %.
- 20 6. The method of claim 1, wherein the gaseous mixture further comprises N₂, He, H₂, Ar, or
any combination thereof.

7. The method of claim 1, wherein the method is a batch process or a continuous flow process.

8. The method of claim 7, wherein when the method is a continuous flow process, the gaseous mixture is in contact with the catalytic mixture at a flow rate of about 40 mL per minute to about 60 mL per minute.

9. The method of claim 1, wherein the Pd is present in the catalyst mixture in an amount of about 1 weight percent to about 5 weight percent.

10. The method of claim 1, wherein the Mn_3O_4 is mesoporous.

11. The method of claim 10, wherein the Mn_3O_4 has an average pore diameter of about 1 nanometer to about 50 nanometers.

12. The method of claim 1, wherein the gaseous mixture further comprises water.

13. The method of claim 12, wherein the water is water vapor or moisture.

14. The method of claim 1, wherein the CO is present in the gaseous mixture in an amount of about 1 volume percent to about 10 volume percent.

15. A method of making a Pd/Mn₃O₄ catalyst, the method comprising:
contacting Mn₃O₄ with a Pd compound to form a reaction mixture;
contacting the reaction mixture with a reducing agent to form a precipitate; and
isolating the precipitate.

5

16. The method of claim 17, wherein the Mn₃O₄ is mesoporous.

17. The method of claim 17, further comprising forming the Mn₃O₄ before contacting the
Mn₃O₄ with the Pd compound, wherein forming the Mn₃O₄ comprises:

- 10 mixing a triblock copolymer, a manganese salt, and a solvent to form a solution;
evaporating the solution to form a product; and
calcining the product.

18. The method of claim 17, wherein the manganese salt is Mn(NO₃)₂, MnCl₂, MnBr₂, MnF₂,
15 MnPO₄, MnSO₄, or any combination thereof.

19. The method of claim 17, wherein the solvent is ethanol, propanol, ether, acetone, ethyl
acetate, water, dimethylformamide, or any combination thereof.

- 20 20. The method of claim 17, wherein the mixing step is performed for about 30 minutes to
about 2 hours.

21. The method of claim 17, wherein evaporating the solution comprises heating to a temperature of about 50 °C to about 80 °C.

5 22. The method of claim 21, wherein the heating step is performed for about 24 hours to about 96 hours.

23. The method of claim 21, wherein evaporating the solution comprises heating until the solvent is substantially evaporated.

10

24. The method of claim 17, wherein calcining the product comprises heating to a temperature of about 300 °C to about 600 °C for about 30 minutes to about 6 hours.

15 25. The method of claim 17, wherein the triblock copolymer is poly(ethyleneglycol)-poly(propyleneglycol)-poly(ethyleneglycol), poly(ethyleneimine)-poly(ethyleneglycol)-poly(ethyleneimine), poly(ethyleneglycol)-polyacetal-poly(ethyleneglycol), polyacetal-poly(ethyleneglycol)-polyacetal, or any combinations thereof.

20 26. The method of claim 15, wherein the palladium compound is Na_2PdCl_4 , H_2PdCl_4 , K_2PdCl_4 , $(\text{NH}_4)_2\text{PdCl}_4$, $\text{Pd}(\text{CH}_3\text{COO})_2$, $\text{Pd}(\text{NO}_3)_2$, PdSO_4 , or any combination thereof.

27. The method of claim 15, wherein contacting Mn_3O_4 with the Pd compound comprises mixing for about 1 hour to about 3 hours.
28. The method of claim 15, wherein the reducing agent is hydrazine, NaBH_4 , KBH_4 , or any combination thereof.
29. The method of claim 15, wherein contacting the reaction mixture with the reducing agent comprises mixing for about 8 hours to about 24 hours.
30. The method of claim 15, wherein isolating the precipitate comprises removing the precipitate from the reaction mixture by centrifugation, filtration, distillation, decantation, or any combination thereof.
31. The method of claim 30, wherein isolating the precipitate further comprises washing the precipitate, and drying the precipitate.
32. A Pd/ Mn_3O_4 catalyst comprising:
a mesoporous Mn_3O_4 support; and
at least one Pd nanoparticle disposed on at least a portion of the mesoporous Mn_3O_4 support, wherein the Pd is present in the Pd/ Mn_3O_4 catalyst in an amount of about 1 weight percent to about 5 weight percent.

33. The catalyst of claim 32, wherein the mesoporous Mn_3O_4 support has an average pore diameter of about 1 nanometer to about 50 nanometers.
34. The catalyst of claim 32, wherein the mesoporous Mn_3O_4 support has an average pore
5 volume of about $0.2 \text{ cm}^3/\text{gram}$ to about $1 \text{ cm}^3/\text{gram}$.
35. The catalyst of claim 32, wherein the mesoporous Mn_3O_4 support has an average BET surface area of about $60 \text{ m}^2/\text{gram}$ to about $150 \text{ m}^2/\text{gram}$.
- 10 36. The catalyst of claim 32, wherein the at least one Pd nanoparticle is disposed on a surface of the mesoporous Mn_3O_4 support, in a pore channel of the mesoporous Mn_3O_4 support, or any combination thereof.
37. The catalyst of claim 32, wherein:
15 the mesoporous Mn_3O_4 support has an average pore diameter of about 1 nanometer to about 50 nanometers;
the mesoporous Mn_3O_4 support has an average pore volume of about $0.2 \text{ cm}^3/\text{gram}$ to about $1 \text{ cm}^3/\text{gram}$; and
the mesoporous Mn_3O_4 support has an average BET surface area of about $60 \text{ m}^2/\text{gram}$ to
20 about $150 \text{ m}^2/\text{gram}$.
38. A system for oxidizing CO to CO_2 , the system comprising:

a gas source configured to supply a gaseous mixture;

a reactor configured to contain a volume of catalyst, wherein the catalyst comprises at

least Pd and Mn_3O_4 , and the reactor comprises an inlet configured to receive the

gaseous mixture such that the gaseous mixture passes through the volume of

5 catalyst, and an outlet configured to allow gaseous mixture that has passed

through the volume of catalyst to exit the reactor, and

the reactor is configured to convert CO to CO_2 at a rate of about 40% to about 100%

when heated to a temperature of about 0 °C to about 60 °C.

10 39. The system of claim 38, wherein the reactor is a fixed-bed tubular reactor.

40. The system of claim 38, wherein the catalyst comprises at least one Pd nanoparticle disposed on at least a portion of a Mn_3O_4 support.

15 41. The system of claim 40, the at least one Pd nanoparticle is disposed on a surface of the mesoporous Mn_3O_4 support, in a pore channel of the mesoporous Mn_3O_4 support, or any combination thereof.

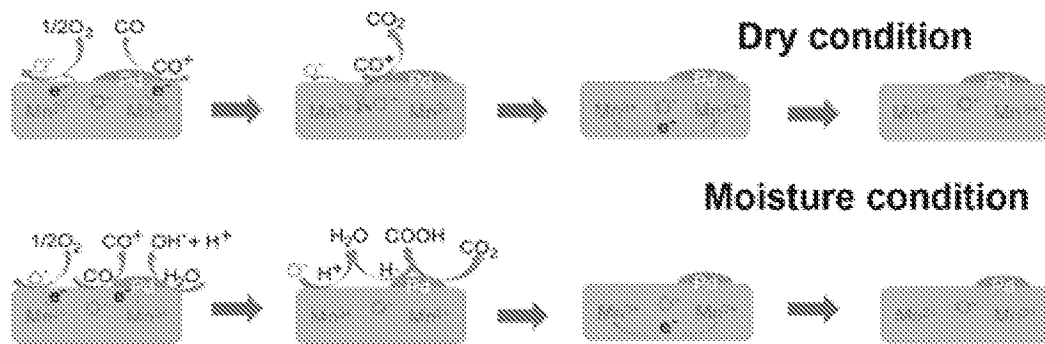


FIG. 1

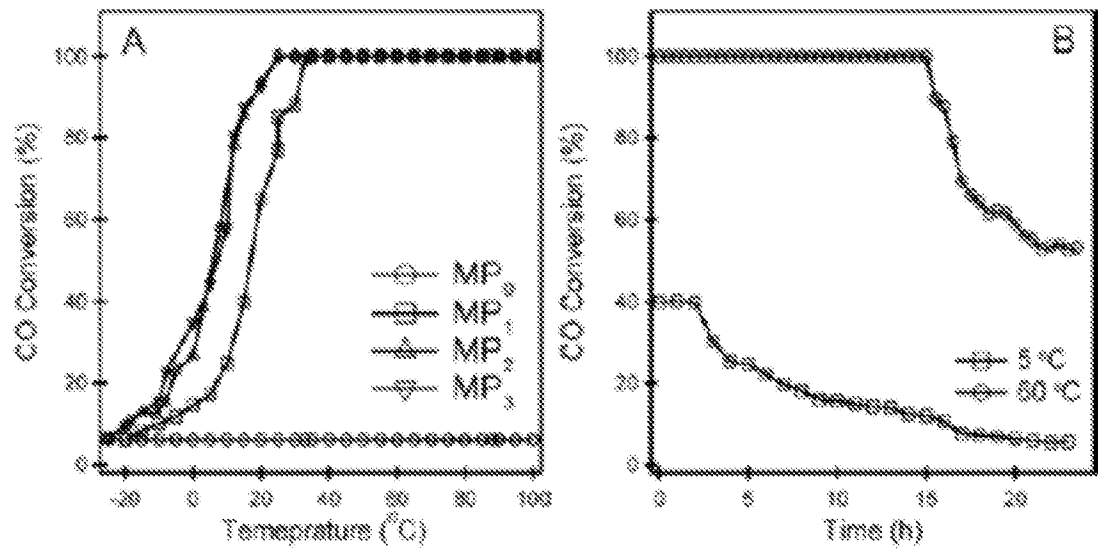


FIG. 2

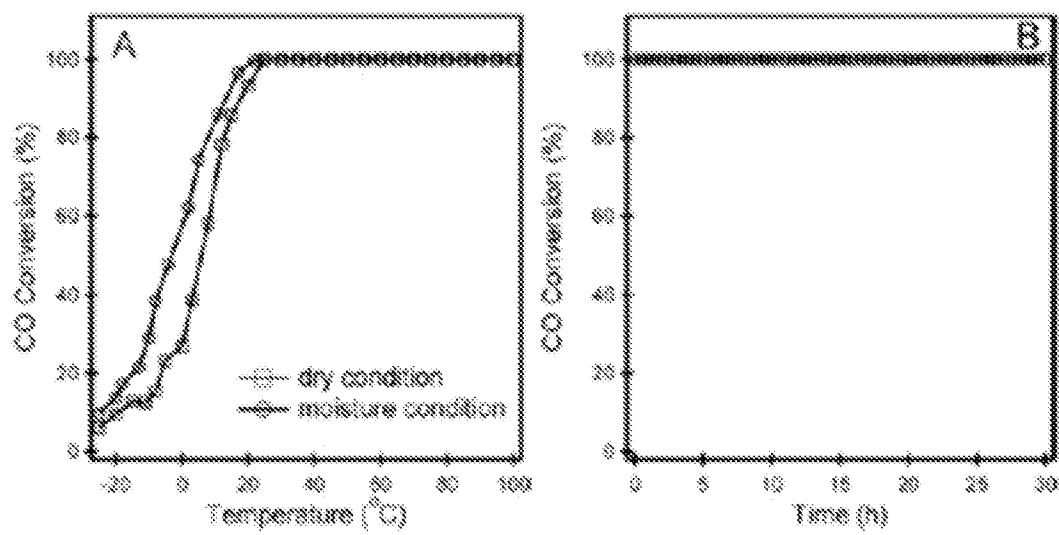


FIG. 3

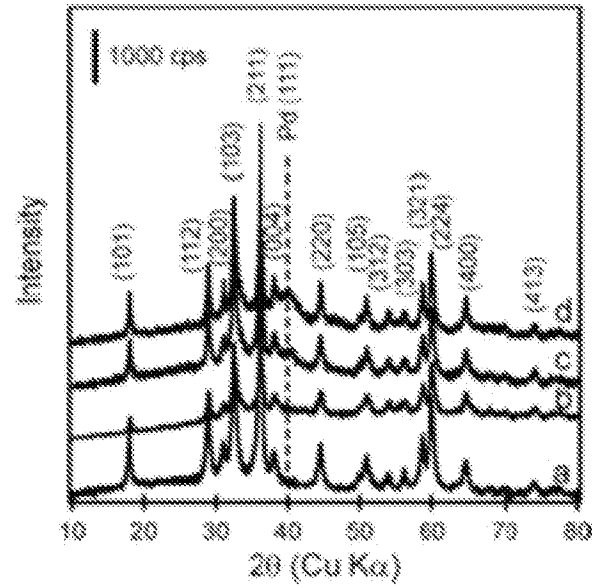


FIG. 4

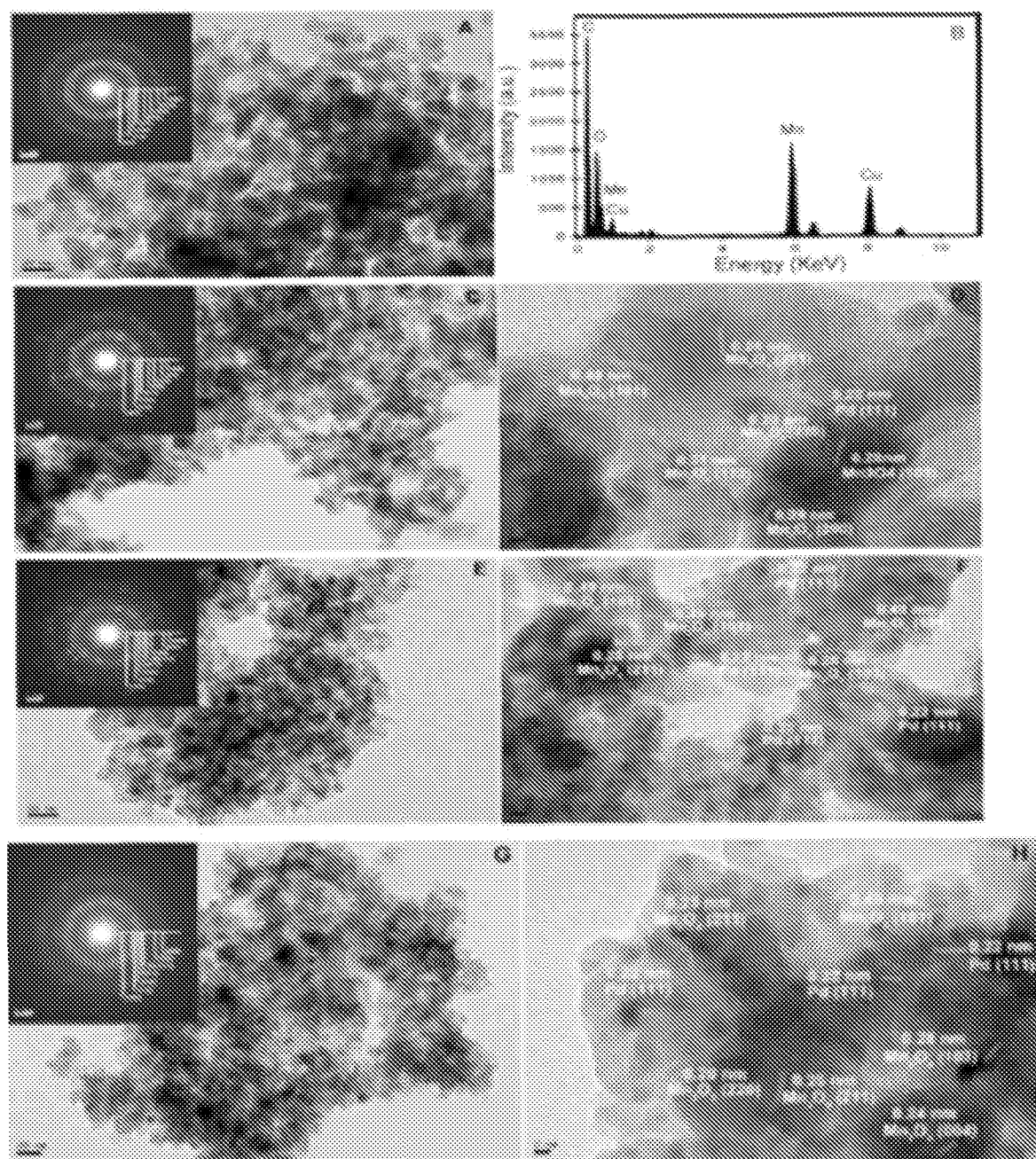


FIG.5

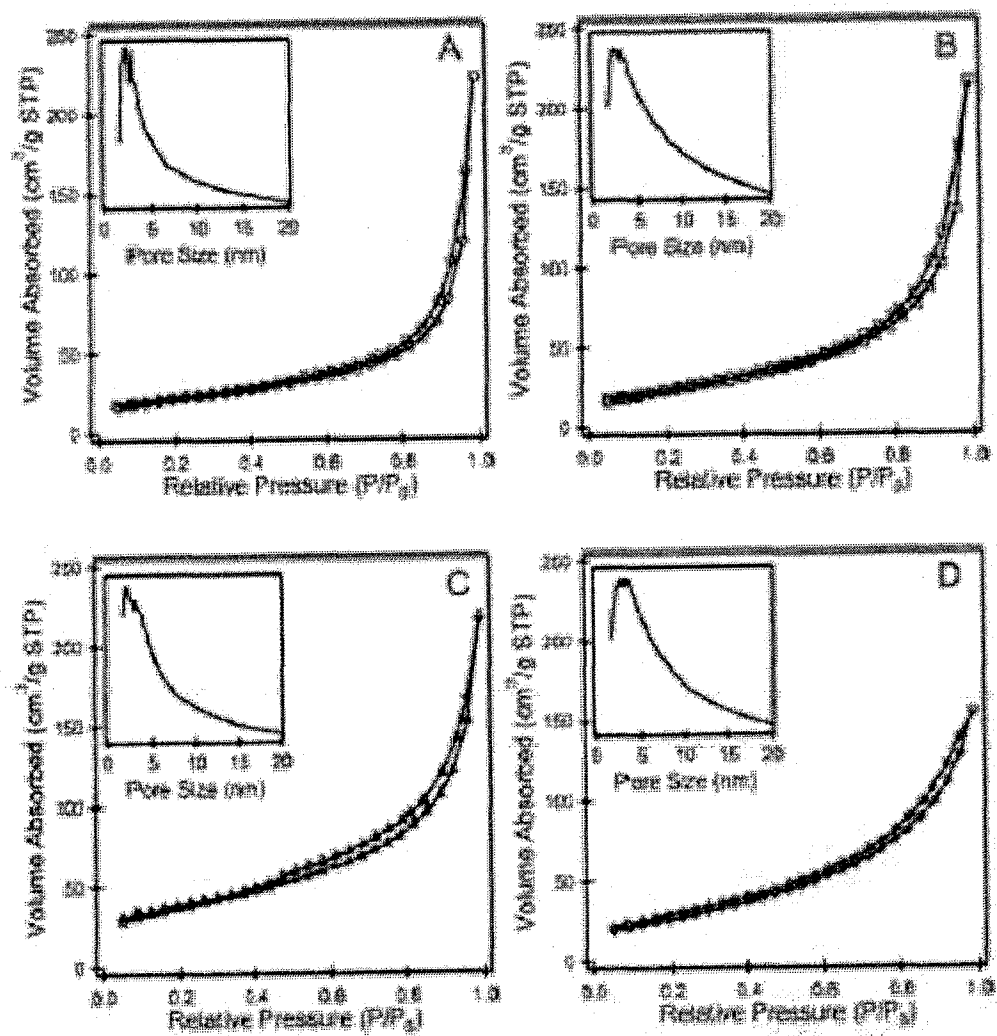


FIG. 6

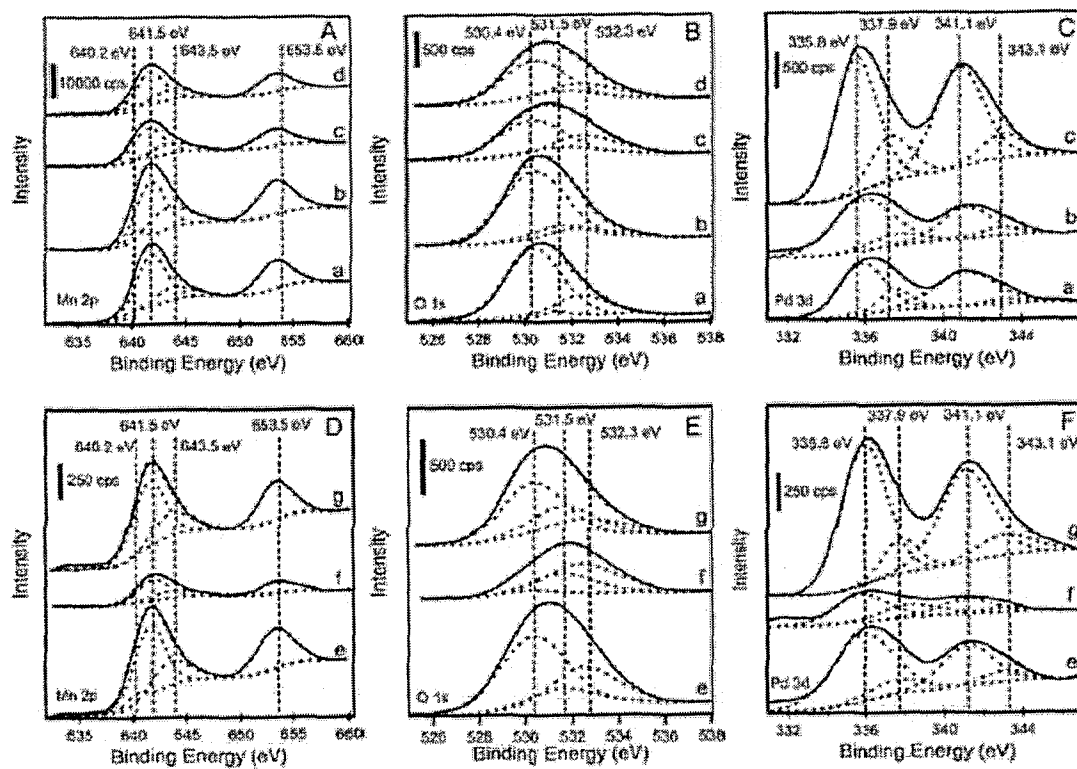


FIG. 7

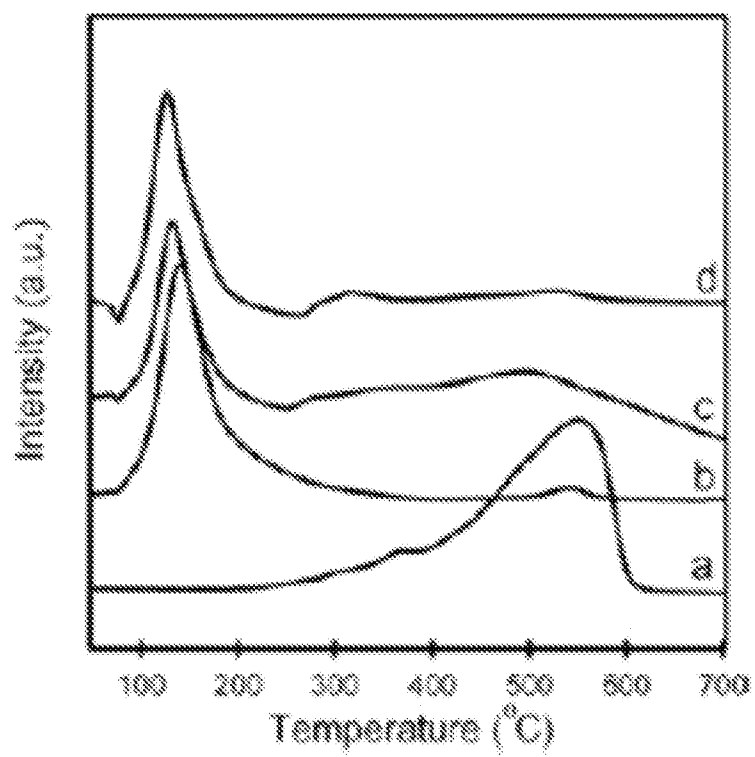


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/071883

A. CLASSIFICATION OF SUBJECT MATTER

B01J 23/44(2006.01)i; B01J 23/656(2006.01)i; B01J 35/10(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT, WPI, EPODOC, CNKI: catalyst, CO oxidation, low temperature, Pd, Mn3O4, support+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GLASPELL, Garry et al. "Nanocatalysis on Supported Oxides for CO Oxidation" <i>TOP. CATAL.</i> , No. vol. 47, 05 February 2008 (2008-02-05), page 23, paragraphs 5, 7, page 29, paragraphs 1-2, figure 9(b)	1-41
Y	CN 101611927 A (HUNAN ZHONGYAN IND. CO., LTD.) 30 December 2009 (2009-12-30) page 5, paragraph 3 to page 6, paragraph 8	1-41
Y	CN 101618350 A (HUNAN ZHONGYAN IND. CO., LTD.) 06 January 2010 (2010-01-06) page 4, paragraphs 2-12	1-41
Y	SALKER, A.V. et al. "Palladium doped manganese dioxide catalysts for low temperature carbon monoxide oxidation" <i>Catalysis Communications</i> , No. vol. 10, 06 June 2009 (2009-06-06), abstract	1-41
A	US 7678734 B2 (FORD GLOBAL TECH. LLC.) 16 March 2010 (2010-03-16) the whole document	1-41
A	EP 1238703 A2 (TOYOTA JIDOSHA KABUSHIKI KAISHA) 11 September 2002 (2002-09-11) the whole document	1-41

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

10 October 2014

Date of mailing of the international search report

06 November 2014

Name and mailing address of the ISA/CN

STATE INTELLECTUAL PROPERTY OFFICE OF THE
P.R.CHINA(ISA/CN)
6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088 China

Authorized officer

JIA,Junlin

Facsimile No. (86-10)62019451

Telephone No. (86-10)62413718

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/071883

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006037610 A1 (HTE AKTIENGESELLSCHAFT THE HIGH THROUGHPUT EXPERIMENTATION COMPANY) 13 April 2006 (2006-04-13) the whole document	1-41

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2014/071883

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN	101611927	A	30 December 2009	CN 101611927 B	25 April 2012
CN	101618350	A	06 January 2010	None	
US	7678734	B2	16 March 2010	EP 1970118 A1	17 September 2008
				US 2008227629 A1	18 September 2008
EP	1238703	A2	11 September 2002	US 2002122755 A1	05 September 2002
				EP 1403218 A1	31 March 2004
				US 7700512 B2	20 April 2010
				EP 1238703 A3	02 May 2003
				US 2006142144 A1	29 June 2006
				JP 2002263501 A	17 September 2002
				US 7094488 B2	22 August 2006
WO	2006037610	A1	13 April 2006	US 2008279738 A1	13 November 2008
				JP 2008515614 A	15 May 2008
				DE 102004048247 A1	06 April 2006
				CN 101068616 A	07 November 2007
				EP 1809416 A1	25 July 2007
				CN 101068616 B	13 July 2011