(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
13 August 2015 (13.08.2015)

WIPO | PCT

(10) **International Publication Number**
WO 2015/117264 A1

(51) **International Patent Classification**:
B01J 37/00 (2006.01)

(21) **International Application Number**:
PCT/CN2014/071872

(22) **International Filing Date**:
7 February 2014 (07.02.2014)

(25) **Filing Language**: English

(26) **Publication Language**: English

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(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: CERIUM DIOXIDE NANOPARTICLES AND METHODS FOR THEIR PREPARATION AND USE

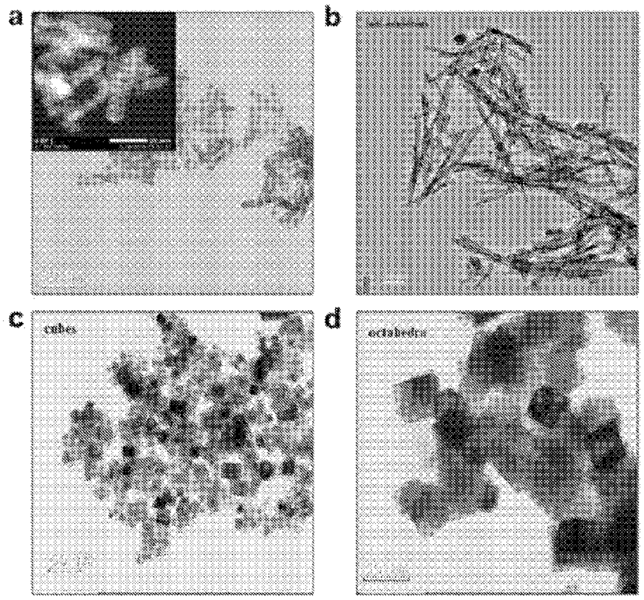

Figure 1

(57) **Abstract**: Nanoparticles and methods for their preparation are described. Porous CeO_2 nanoparticles may be made by contacting $Ce(NO_3)_3$ with a base to form a mixture, and converting the mixture into a composition including one or more porous CeO_2 nanoparticles. Nanoparticles may be made by contacting $Ce(NO_3)_3$ with a base to form a mixture including the nanoparticles. Porous CeO_2 nanoparticles may have a high oxygen vacancy concentration, a high specific surface area, a high oxygen storage capacity, and/or a high specific Ce^{3+} ratio. The porous CeO_2 nanoparticles may be used as a co-catalyst in a catalyst system or as a catalyst carrier.

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CERIUM DIOXIDE NANOPARTICLES AND METHODS FOR THEIR PREPARATION AND USE

BACKGROUND

[1] The reversible conversion between Ce^{4+} and Ce^{3+} existing in the structure of fluorite CeO_2 endows CeO_2 (cerium dioxide; cerium (IV) oxide) nanomaterial with excellent oxygen storage and release performance and oxidation-reduction ability. For this reason, CeO_2 nanomaterial is widely applied in high-tech fields such as, for example, catalysts, co-catalysts, catalyst carriers, water pollution purification, ultraviolet absorbers, three-way catalysts, oxygen sensors, solid oxide fuel cells, glass polishing, and electrode materials.

[2] For applications such as automobile exhaust treatment, Oxygen Storage Capacity (OSC) is an important parameter index for assessing catalysts. The OSC of pure CeO_2 is relatively small (less than 360 μmol/g). A common method for increasing OSC is CeO_2 doping. Doping with Zr is studied most widely at present. The OSCs of most doped CeO_2 are 500-700 μmol O_2/g. When CeO_2 serves as an active component of a catalyst, a co-catalyst, or a catalyst carrier, the control of its surface defects or acid and basic sites has a great impact on the catalytic material. Therefore, CeO_2 material with a higher OSC and controllable surface acid and basic sites is desirable.

SUMMARY

[3] In an embodiment, a method of making one or more porous CeO_2 nanoparticles includes contacting $Ce(NO_3)_3$ and a base at a pressure and temperature to form a mixture, and converting the mixture into a composition including one or more porous CeO_2 nanoparticles.

[4] In an embodiment, a method of making one or more nanoparticles includes contacting $Ce(NO_3)_3$ and a base at a pressure and temperature to form a mixture comprising the one or more nanoparticles.

[5] In an embodiment, at least one porous CeO_2 nanoparticle has high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, a high specific surface Ce^{3+} ratio, or combinations thereof.

[6] In an embodiment, a catalyst system includes at least one first catalyst and at least one co-catalyst, wherein the co-catalyst includes at least one porous CeO_2 nanoparticle.

[7] In an embodiment, a catalyst system includes a catalyst supported on a carrier, wherein the carrier includes at least one porous CeO_2 nanoparticle.

[8] In an embodiment, one or more nanoparticles are prepared by a method including contacting $Ce(NO_3)_3$ and base at a pressure and temperature to form a mixture including one or more nanoparticles.

BRIEF DESCRIPTION OF THE DRAWINGS

[9] The drawings submitted herewith show some embodiments or features of some embodiments encompassed by the disclosure. The drawings are meant to be illustrative and are not intended to be limiting.

[10] Figure 1 shows the TEM images of the as-prepared porous CeO_2 nanorods, nonporous CeO_2 nanorods, CeO_2 nanocubes, and CeO_2 nano-octahedrons.

[11] Figure 2 shows the performance parameters of porous CeO_2 nanorods subjected to different treatments.

[12] Figure 3 shows CO oxidation performance catalyzed by porous CeO_2 nanorods.

[13] Figure 3(a) shows a comparison between porous CeO_2 nanorods (triangle symbols) and nonporous CeO_2 nanorods (round symbols). The x-axis is temperature in °C. The y-axis is CO conversion in percent.

[14] Figure 3(b) shows CO oxidation catalyzed by nonporous CeO_2 nanorods (square symbols), cubes (round symbols), and octahedrons (triangle symbols). The x-axis is temperature in °C. The y-axis is CO conversion in percent.

[15] Figure 3(c) shows CO oxidation catalyzed by porous CeO_2 nanorods treated hydrothermally at different temperatures (square symbols = 120 °C, round symbols = 140 °C, rightside up triangle symbols = 160 °C, upside down triangle symbols = 180 °C, and left facing triangle symbols = 200 °C). The x-axis is temperature in °C. The y-axis is CO conversion in percent.

[16] Figure 3(d) shows CO oxidation catalyzed by porous CeO_2 nanorods treated by high temperature annealing (square symbols = 200 °C, round symbols = 300 °C, rightside up triangle symbols = 400 °C, and upside down triangle symbols = 500 °C). The x-axis is temperature in °C. The y-axis is CO conversion in percent.

[17] Figure 4 shows a summary of OSC and BET surface areas of CeO_2 based nanostructures.

DETAILED DESCRIPTION

[18] 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.

[19] 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."

[20] The described technology generally relates to nanoparticles and methods for their preparation and use. The nanoparticles may be made by contacting $Ce(NO_3)_3$ and a base at a pressure and temperature to form a mixture of one or more nanoparticles. This mixture can be converted into a composition including one or more porous CeO_2 nanoparticles. In some embodiments, the porous CeO_2 nanoparticles have high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, high specific surface Ce^{3+} ratio, or a combination thereof. In some embodiments, the porous CeO_2 nanoparticles are used in a catalyst system including at least one first catalyst and at least one co-catalyst, wherein the co-catalyst includes at least one porous CeO_2 nanoparticle. In some embodiments, the porous CeO_2 nanoparticles are used in a catalyst system including wherein a catalyst is supported on a carrier, and the carrier includes at least one porous CeO_2 nanoparticle.

[21] As described herein, CeO_2 material with a higher OSC and/or controllable surface acid and basic sites is provided. The preparation of porous CeO_2 nanorods is achieved by a simple scheme in which the conventional hydrothermal method is improved. In some embodiments, the nanomaterial made according to a method described herein has a very high oxygen vacancy concentration, and therefore a high OSC. In some embodiments, the OSC is about 4 times as much as that of conventional CeO_2 nanomaterial. In some embodiments, the nanomaterial made according to a method described herein additionally has a high specific surface area and/or a high specific surface Ce^{3+} ratio. These characteristics provide CeO_2 materials produced according to methods described herein with unique advantages in oxidation reactions and/or reactions catalyzed by a Lewis Base. In some embodiments, the control of surface oxygen vacancy and Ce^{3+} concentration can be achieved by post-treatment. In some embodiments, the porous structure of the CeO_2 material has good stability while maintaining the fluorite structure as unchanged. Thus, in some embodiments, the structure will not collapse when exposed to a high temperature, for example a temperature of 600 °C, for a long period of time.

[22] Disclosed herein are nanoparticles, and methods for their preparation and use. The nanoparticles may be prepared by any method described herein. In terms of material preparation, the present method is simple and cost-effective. The chemicals needed are only low-cost cerous nitrate and sodium hydroxide. The laboratory work shows that the cost for preparing porous CeO_2 nanorods is even lower than that for preparing porous SiO_2 materials under the same laboratory conditions.

[23] CO oxidation reactions exist in many fields of industrial production, such as automobile exhaust treatment, diesel engine exhaust treatment, purification of hydrogen fuel in proton exchange membrane fuel cells, prevention of platinum electrode of methanol fuel cells from poisoning, water-gas shift reaction, methanol synthesis, methane conversion, methanol/ethanol steam reforming for hydrogen production, and hydrocarbon reforming. Moreover, a CO oxidation reaction is often used as a probe reaction for an oxidation catalyst to reveal the relationship between catalyst performances and structure, wherein CeO_2 material is mainly applied in the form of catalyst carrier in such a reaction. Various active components, for example, noble metals such as Pt, Au, and Ru, or non-noble metal oxides such as CuO, NiO, and Co_3O_4, can be highly dispersed in this novel porous CeO_2 nanomaterial, and the porous structure of this CeO_2 material can enhance the synergistic effect between active components and carriers; meanwhile, in combination with the good oxidation-reduction performances of this porous CeO_2 material, such CeO_2 material, as an active co-agent, can significantly improve the CO oxidation ability of the corresponding catalyst system, thereby effectively improving the corresponding reaction performances.

[24] Cyclohexanone is a main raw material in the industrial production of Nylon-6 and Nylon-6,6. The demand for lowering costs and reducing energy-consumption promotes extensive research on the method for producing cyclohexanone from phenol through hydrogenation. A noble metal, for example, Pd, is loaded onto this type of porous CeO2 nanomaterial. In one aspect, the high pore density and large specific surface area can greatly stabilize the existence of the noble metal active components. In another aspect, the increase in alkalinity on the surface of such materials can also promote electron enrichment at Pd active sites.

[25] Aldehydes and ketones are significant compounds for synthesizing fine chemicals, and they are mainly converted from the oxidation of alcohols. The excellent oxidation-reduction performances of this type of CeO2 material facilitate the direct oxidation of alcohols into aldehydes and ketones by corresponding catalysts. The porous structure can stabilize the activated active components, and meanwhile the rapid flow of oxygen on the surface is beneficial to the re-oxidation of the active components after reaction.

[26] The production of unsaturated alcohols from α,β-unsaturated aldehydes through hydrogenation is a significant reaction for producing pharmaceuticals, agricultural chemicals and perfume compounds. C=C is a chemical bond more stable than C=O. For example, in crotonaldehyde and citral, the oxygen vacancies located at the interface between CeO_2 and active metal components can accelerate the induction of C=O bond activation due to the fact that the porous structure on the surface of this material enhances the metal-carrier interactions between CeO_2 carrier and active components.

[27] Acetals are widely applied in the production of cosmetics, foods and flavor additives, pharmaceuticals and polymers in the form of perfume, and acetals are obtained mainly by condensation of carbonyl compounds. The Lewis-Acid sites formed by a high concentration of Ce^{3+} on the surface of this novel CeO_2 porous material can accelerate the activation of carbonyl groups by synergistic effects.

[28] The large amount of polluted water discharged from pharmaceutical factories, chemical plants and residential areas can cause water eutrophication after it enters water body and promote abnormal growth of various aquatic organisms, so it is extremely harmful. CeO_2 material is a semiconductor itself, which, in combination with the good valence alternation feature of this novel porous structure, makes this porous material have excellent photocatalytic performances to effectively inhibit simple complexation of electron-vacancy pairs and almost non-selectively oxidize organic compounds, thus playing an important role in polluted water treatment.

[29] The industrial waste water from dye, pharmaceutical, petrifaction and plasticizer productions comprises a large amount of phenol. This type of waste water has serious pollution to the environment, and has great toxicity to human and aquatic organisms. Low concentration of phenol can be oxidized by catalytic wet oxidation. CeO_2 material has excellent ability of oxidizing phenol, which, in combination with the low cost, good structural stability and recyclability of this novel porous structure, makes this novel CeO_2 material play an important role in the treatment of waste water containing phenol.

[30] In some embodiments, a method of making one or more porous CeO_2 nanoparticles includes contacting $Ce(NO_3)_3$ and a base at a pressure and temperature to form a mixture, and converting the mixture into a composition including one or more porous CeO_2 nanoparticles.

[31] In some embodiments, a method of making one or more nanoparticles includes contacting $Ce(NO_3)_3$ and a base at a pressure and temperature to form a mixture comprising one or more nanoparticles. In some embodiments, the method further comprises converting the mixture into a composition including one or more porous CeO_2 nanoparticles.

[32] In some embodiments, at least one porous CeO_2 nanoparticle has one or more of high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, high specific surface Ce^{3+} ratio, or combinations thereof.

[33] In some embodiments, a catalyst system includes at least one first catalyst and at least one co-catalyst, wherein the co-catalyst includes at least one porous CeO_2 nanoparticle. In some embodiments, the first catalyst may be CeO_2-ZrO_2, CeO_2-TiO_2, CeO_2-CdS, or combinations thereof.

[34] In some embodiments, a catalyst system includes a catalyst supported on a carrier, wherein the carrier includes at least one porous CeO_2 nanoparticle. In some embodiments, the catalyst may be Pt, Au, Pd, Ni, Ru, NiO, CuO, or a combination thereof.

[35] The nanoparticles of any of the embodiments may be prepared by any of the methods described herein.

[36] In any of the embodiments described herein, the base may be NaOH, KOH, or combinations thereof. In some embodiments, the base is NaOH.

[37] In any of the embodiments described herein, the ratio of $Ce(NO_3)_3$ to base may be about 1:80 to about 1:200. In some embodiments, the ratio of $Ce(NO_3)_3$ to base is about 1:120.

[38] In any of the embodiments described herein, the pressure may be about 1.0 atmospheres to about 1.5 atmospheres.

[39] In any of the embodiments described herein the temperature may be about 100 °C. In some embodiments, the temperature is 100 °C.

[40] In any of the embodiments described herein, the mixture may include at least one of CeO_2 and $Ce(OH)_3$. In some embodiments, the mixture includes CeO_2 and $Ce(OH)_3$.

[41] In any of the embodiments described herein, the method of making nanoparticles may include washing the mixture to remove excess base after contacting $Ce(NO_3)_3$ and the base. In some embodiments, distilled water is used to wash the mixture. In some embodiments, the washing results in the mixture having a neutral pH value.

[42] In any of the embodiments described herein, the method of making nanoparticles may include dispersing the mixture in a liquid. In some embodiments, the liquid includes water. In some embodiments, the liquid includes a hydrophilic solvent. In some embodiments, the liquid includes an alcohol, a ketone, N-N-dimethylformamide, or combinations thereof.

[43] In any of the embodiments described herein, the method of making nanoparticles may include converting the mixture created by contacting $Ce(NO_3)_3$ and a base at a pressure and temperature into a composition including one or more porous CeO_2 nanoparticles. In some embodiments, the mixture is converted into a composition including one or more porous CeO_2 nanoparticles by dehydrating the mixture. In some embodiments, a hydrothermal method is used to dehydrate the mixture. In some embodiments, the hydrothermal method uses an autoclave. In some embodiments, the autoclave is set at a temperature of about 160 °C to about 200 °C. In some embodiments, the autoclave is set at a temperature of about 160 °C. In some embodiments, the mixture is in the autoclave for about 12 hours to about 24 hours. In some embodiments, the mixture is in the autoclave for about 12 hours. In some embodiments, the mixture is converted into a composition comprising one or more porous CeO_2 nanoparticles by calcination. In some embodiments, the calcination occurs at a temperature of about 200 °C to about 600 °C. In some embodiments, the calcination occurs at a temperature of about 300 °C.

[44] Any of the foregoing embodiments may be used to make the nanoparticles described herein.

[45] In any of the embodiments described herein, the nanoparticles may be a mixture of CeO_2 and $Ce(OH)_3$. In some embodiments, the nanoparticles are substantially CeO_2. In some embodiments, the nanoparticles are CeO_2. In some embodiments, the nanoparticles have an average length of about 40 nm to about 80 nm. In some embodiments, the nanoparticles have an average diameter of about 5 nm to about 8 nm. In some embodiments, the nanoparticles are rod-shaped. In some embodiments, the nanoparticles are porous. In some embodiments, the nanoparticles are non-porous.

[46] In any of the embodiments described herein, the nanoparticles may be porous CeO_2 nanoparticles. In some embodiments, the porous CeO_2 nanoparticles have an average length of about 40 nm to about 80 nm. In some embodiments, the porous CeO_2 nanoparticles have an average diameter of about 5 nm to about 8 nm. In some embodiments, the porous CeO_2 nanoparticles have one or more of high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, high specific surface Ce^{3+} ratio, or combinations thereof. In some embodiments, the porous CeO_2 nanoparticles may have an oxygen vacancy concentration that is larger than the oxygen vacancy concentration of nonporous CeO_2 nanoparticles. In some embodiments, the porous CeO_2 nanoparticle may have a specific surface area of at least about 95 m^2/g. In some embodiments, the porous CeO_2 nanoparticle may have a specific surface area of 95 m^2/g to 150 m^2/g. In some embodiments, the porous CeO_2 nanoparticles have a specific surface area of about 100 m^2/g to about 150 m^2/g. In some embodiments, the porous CeO_2 nanoparticles have a specific surface area of about 95 m^2/g, about 100 m^2/g, about 105 m^2/g, about 141 m^2/g, or about 150 m^2/g, or any number between any of these values, or any range of numbers between any of these values or beginning or ending with any of these values, inclusive. In some embodiments, the porous CeO_2 nanoparticles may have an oxygen storage capacity of at least about 700 μmol O_2/g. In some embodiments, the porous CeO_2 nanoparticles may have an oxygen storage capacity of about 700 μmol O_2/g to about 900 μmol O_2/g. In some embodiments, the porous CeO_2 nanoparticles may have an oxygen storage capacity of about 800 μmol O_2/g to about 900 μmol O_2/g. In some embodiments, the porous CeO_2 nanoparticles may have an oxygen storage capacity of about 900 μmol O_2/g. In some embodiments, the porous CeO_2 nanoparticles may have an oxygen storage capacity of about 700 μmol O_2/g, about 715 μmol O_2/g, about 800 μmol O_2/g, about 840 μmol O_2/g, or about 900 μmol O_2/g, or any number between any of these values, or any range of numbers between any of these values or beginning or ending with any of these values, inclusive. In some embodiments, the porous CeO_2

nanoparticles may have a specific surface Ce^{3+} ratio of at least about 9 %. In some embodiments, the porous CeO_2 nanoparticles may have a specific surface Ce^{3+} ratio of about 9 % to about 33 %. In some embodiments, the porous CeO_2 nanoparticles may have a specific surface Ce^{3+} ratio of about 9 % to about 21 %. In some embodiments, the porous CeO_2 nanoparticles may have a specific surface Ce^{3+} ratio of about 19 % to about 33 %. In some embodiments, the porous CeO_2 nanoparticles may have a specific surface Ce^{3+} ratio of about 9 %, about 9.21 %, about 19 %, about 21 %, about 30.8 %, or about 33 %, or any number between any of these values, or any range of numbers between any of these values or beginning or ending with any of these values, inclusive.

[47] In any of the embodiments described herein, there may be at least one active component dispersed in the porous CeO_2 nanoparticles. In some embodiments, the active component may be at least one noble metal, at least one metal oxide, at least one bi-metal, at least one triple-metal, or combinations thereof. In some embodiments, the noble metal may be ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, mercury, rhenium, silver, copper, or combinations thereof. In some embodiments, the metal oxide may be CuO, NiO, Co_3O_4, or combinations thereof. In some embodiments, the bi-metal may be PtPd, AuPd, or combinations thereof. In some embodiments, the bi-metal may be two metals selected from Ni, Co, Au, Ag, Cu, Fe, Pt, Pd, Rh, Ru, and Ir. In some embodiments, the triple-metal may be CoNiPt, CuPdAu, or combinations thereof. In some embodiments, the triple-metal may be three metals selected from Ni, Co, Au, Ag, Cu, Fe, Pt, Pd, Rh, Ru, and Ir.

EXAMPLES

Example 1: Material Synthesis

[48] Porous CeO_2 nanorods were synthesized by a two-step hydrothermal method. The amount of the Ce^{3+} in the precursor and the pressure aid in the reaction of producing precursors. The two-step hydrothermal method includes first mixing $Ce(NO_3)_3$ and NaOH to obtain the rod-shaped precursor nanostructures of a mixture of $Ce(OH)_3$ and CeO_2. The pressure of this step was controlled between 1 atm and 1.5 atm. At the end of this step, any excess NaOH was washed off. Secondly, the mixture was dehydrated to obtain the porous CeO_2 nanorods through either the second hydrothermal treatments or high temperature calcination. A reactor was designed to precisely control the reaction conditions of the first step in the low pressure regime. The pressure control in the first-step hydrothermal process aids in producing the porous CeO_2 with high surface area and high OSC.

Example 2: Material Characterization/Performances

[49] Figure 1 shows the TEM images of the as-prepared porous CeO_2 nanorods, nonporous CeO_2 nanorods, CeO_2 nanocubes, and CeO_2 nano-octahedrons. The basic performances of the materials were characterized by various methods. The specific data are listed in the table in Figure 2. The specific surface area measurement was conducted on ASAP 2020 (Micromeritics, Inc.; Norcross, GA, USA). The OSC was measured by using CHEMBET-3000 (Quantachrome, Inc.; Boynton Beach, FL, USA). The surface Ce^{3+} ratio was obtained by XPS (Thermo Scientific K-Alpha; Thermo Fisher Scientific; Waltham, MA, USA). It can be seen from the table that the porous CeO_2 nanorods obtained from either hydrothermal treatment (HY) or high-temperature calcination (delta symbol) have very high specific surface area (BET), wherein the porous CeO_2 nanorods hydrothermally treated at 160 °C have the highest specific surface area (141 m^2/g), the highest OSC, and the highest surface Ce^{3+} ratio. In terms of hydrothermal treatment and high-temperature calcination schemes, the porous CeO_2 nanorods obtained from the hydrothermal treatment have a larger specific surface area, a higher OSC and a higher surface Ce^{3+} ratio. The assays of these performances were achieved by repeating the measurements many times. This means that the surface performances of the porous CeO_2 nanorods obtained by the herein described method can become controllable by treatments. This provides a good research platform for regulating catalytic materials and reactions. Based on this, CO oxidation reaction (the main reaction in automobile exhaust treatment) was used as a characterization reaction to verify the catalytic activity of the porous CeO_2 nanorods.

[50] To verify the catalytic activity of the as-prepared porous CeO_2 nanorods, nonporous CeO_2 nanorods, CeO_2 nanocubes and CeO_2 nano-octahedrons were also prepared for comparative experiments. All the experiments were carried out under the same catalytic conditions. Specific catalytic parameters are as follows:

[51] A quartz reactor with an inner diameter of 4 mm was filled with 250 mg of a catalyst with a particle size of 60-100 mesh in the middle section. Both ends of the reactor bed were blocked with silica wool. Then, a K-shape thermocouple was placed at the middle of the catalyst bed. After filling, a reaction gas, which consists of 1% O_2, 1% CO and a balance of Ar, was charged at a flow rate of 50 ml/min.

[52] The catalysis results are shown in Figure 3. In terms of the catalytic performances of the nonporous and porous CeO_2 nanorods, the porous CeO_2 nanorods hydrothermally treated at 160 °C oxidized CO into CO_2 completely at 320 °C, whereas the nonporous CeO_2 nanorods could not oxidize 99% CO into CO_2 until the temperature reached about 420 °C. In addition, the CeO_2 nanocubes completely oxidized CO at a temperature above 420 °C, while the CeO_2 nano-octahedrons only converted 33% CO at 420 °C. The oxidation catalytic performances of the nonporous CeO_2 nanorods, CeO_2 nanocubes and CeO_2 nano-octahedrons were in accordance with those reported in the prior references. It is demonstrated that the porous CeO_2 nanorods prepared by the herein described method have very high catalytic activity in oxidizing CO. The enhanced catalytic activity is mainly derived from the unique performance of high OSC of the porous CeO_2 nanorods.

[53] The CO oxidation catalytic performances of the porous CeO_2 nanorods subjected to different treatments were also compared. Figure 3(c) shows the catalytic performances of the porous CeO_2 nanorods subjected to hydrothermal treatment. It can be seen from the figure that the nanorods hydrothermally treated at 160 °C and 180 °C have the highest CO oxidation catalytic performances. The porous CeO_2 nanorods hydrothermally treated at 180 °C completely oxidize CO at 280 °C, which is in accordance with the results of OSC and specific surface area of the catalyst. However, the catalytic performances of the porous CeO_2 nanorods subjected to high-temperature calcination are inferior to those of the porous CeO_2 nanorods subjected to hydrothermal treatment. For the calcinated samples, the catalytic performances are different at the initial stage, but CO is almost completely oxidized at 420 °C. In terms of the two treatment methods, the porous CeO_2 nanorods subjected to hydrothermal treatment (at 160 °C and 180 °C) have reduced the temperature at which CO is completely oxidized by 140 °C. This demonstrates the superior catalytic performances of the porous CeO_2 nanorods subjected to hydrothermal treatment.

[54] Due to high OSC, high specific surface area and controllable surface performances, porous CeO_2 nanorods can be widely applied in many catalytic reactions, such as organic reactions catalyzed by Lewis acid-base under research, WGS reactions, steam reforming of CH_4 and dry reforming of methane. Great progress has been made in laboratories for dry reforming of methane (DRM). DRM is a significant reaction in which CO_2 is reused to produce CO and H_2 under catalysis, and it can also achieve the objective of reducing problematic gases CO_2 and CH_4. However, this reaction is an endothermic reaction and usually occurs at 500-800 °C. The existing main problems of this reaction are thermal stability of metal catalyst carrier, high-temperature agglomeration of metal catalyst on carrier surface, carbon deposition and inhibition of side reactions. The experiments show that the CeO_2 nanorods have advantages in stabilizing metal catalysts, inhibiting RWGS reactions and carbon deposition. The catalytic performance of 3% loaded Pt/Porous CeO_2 nanorods was reduced by only 4% in a 72 hour continuous reaction at a reaction temperature of 800 °C. The carbon weight percentage of the carbon in the catalysts after 72 hours continuous reaction was determined to be only 0.3 wt % by the thermogravimetric analysis, indicating the remarkable ability of the catalysts to prevent the carbon deposition during the DRM reactions.

[55] Improvement in OSC and regulation of surface performance of CeO_2 material as a catalytic material carrier, a co-catalyst and an active component has always been of considerable research interest. Preparation methods can radically determine the performance parameters of the materials and demonstrate their performances. In previous studies, the maximum OSC of pure CeO_2 nanostructure can reach 357 μmol/g. A common method is to introduce Zr into CeO_2 materials. The addition of Zr can not only increase the activity of oxygen in CeO_2, improve the bulk phase characteristics of CeO_2, reduce the reduction temperature of Ce^{4+} and enhance the thermal stability, but also significantly improve the oxygen storage capability of the catalyst. Currently, the OSCs of Zr-doped CeO_2 reported in references are typically less than 750 μmol/g. Only one reference reports that the OSC of CeO_2 has reached 930 μmol/g (see Figure 4). The CeO_2 nanostructures as well as their OSCs and specific surface areas after doping as reported in references are summarized in the table in Figure 4.

[56] The specific surface area of the as-prepared porous CeO_2 nanorods is not the largest. However, the porous CeO_2 nanorods have very good thermostability. In the research results on Zr-doped CeO_2, although the initial specific surface area of the sample CZ14 (281 m^2/g) is larger than that of the porous CeO_2 nanorods as prepared by methods disclosed herein, the specific surface area of CZ14 dramatically decreases to 66 m^2/g after being calcinated at 500 °C, while the specific surface area of the porous CeO_2 nanorods as prepared by methods disclosed herein can still be 96 m^2/g after being calcinated at 500 °C for 4 hours, with a slight decrease. Additionally, the sample CZ14 only has an OSC of 104.5 μmol O^2/g at 500 °C, while the porous CeO_2 nanorods as prepared by methods disclosed herein have an OSC as high as 715.6 μmol O^2/g even after treatment at 500 °C. In further comparison of catalytic performances, the CO oxidation ignition temperature T_{50} (defined as the temperature at which 50% of CO is converted into CO_2) of the sample CZ14 is at least higher than 390 °C, while the T_{50} of the porous CeO_2 material as prepared by methods disclosed herein is only 230 °C.

Example 3: Treatment of Automobile Exhaust

[57] Porous CeO_2 nanorods are synthesized by the two-step hydrothermal method described in Example 1 and placed in an automobile exhaust system. In the system, the porous CeO_2 nanorods are exposed to exhaust from the engine combustion. Exhaust gases are allowed to contact the porous CeO_2 nanorods, thereby oxidizing CO to CO_2.

Example 4: Treatment of Diesel Engine Exhaust

[58] Porous CeO_2 nanorods are synthesized by the two-step hydrothermal method described in Example 1 and placed in a diesel engine exhaust system. In the system, the porous CeO_2 nanorods are exposed to exhaust from the engine combustion. Exhaust gases are allowed to contact the porous CeO_2 nanorods, thereby oxidizing CO to CO_2. Generally, the thermal stability of the catalysts is important for this purpose since the reaction is performed at high temperatures. Herein, the thermal stability of the porous CeO_2 nanorods with a surface area of 141 m^2/g and the nonporous CeO_2 nanorods were examined at high temperatures. After 600 °C calcination in air for 4 hours, 84.4% and 77.2% surface areas were preserved for the porous and nonporous CeO_2 nanorods. Raising the temperature to 800 °C, the surface area of the porous CeO_2 nanorods maintained 61% of that of as synthesized. In contrast, only 29% of surface area was obtained for the nonporous CeO_2 nanorods. The results indicated the excellent thermal stability of the porous CeO_2 nanorods, which have promising applications for many high temperature processes including the treatments on the diesel engine exhaust.

Example 5: Production of Cyclohexanone from Phenol through Hydrogenation

[59] Porous CeO_2 nanorods are synthesized by the two-step hydrothermal method described in Example 1. The noble metal Pd is loaded onto the porous CeO_2 nanorods. Since porous CeO_2 nanorods with a stronger basicity, they are very suitable as the support for palladium nanoparticles and enhance the capacity activity. The strong interaction between Pd nanocatalysts and porous CeO_2 nanorods with strong basicity can significantly increase the stability of the Pd nanoparticles. Moreover, the feature of the strong basicity of the porous CeO_2 nanorods will provide more electrons to Pd nanoparticles and hence increase catalytic activity for converting phenol to cyclohexanone. The high Ce^{3+} fraction of the porous CeO_2 nanorods favors the nonplanar-adsorption of the phenol on the surface of the catalysts and will increase the selectivity of the products to cyclohexanone. The reaction could be performed in gas-phase or liquid phase using ethanol as the solvent.

Example 6: Water Pollution Treatment

[60] Porous CeO_2 nanorods are synthesized by the two-step hydrothermal method described in Example 1. A phenol-containing waste stream is allowed to flow through or over the porous CeO_2 nanorods. The porous CeO_2 nanorods oxidize the phenolic compounds. Thus, harmful organic compounds are oxidized, thereby reducing the pollution in the waste stream.

[61] 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 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.

[62] 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.

[63] 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.

[64] 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.

[65] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (for example, bodies of the appended claims) are generally intended as “open” terms (for example, 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,” et cetera). 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. 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 indefinite articles such as "a" or "an" (for example, “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 (for example, the bare recitation of "two recitations," without other 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, et cetera” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (for example, “ 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 together, and/or A, B, and C together, et cetera). In those instances where a convention analogous to “at least one of A, B, or C, et cetera” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (for example, “ 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, et cetera). It will 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.”

[66] 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 described in terms of any individual member or subgroup of members of the Markush group.

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

[68] The following terms shall have, for the purposes of this document, the respective meanings set forth below.

[69] As used herein, “a neutral pH value” refers to a pH of around 7.

[70] As used herein, “a hydrothermal method” refers to a method of synthesis of materials that depends on the solubility of precursors in hot water under high pressure.

[71] As used herein, “oxygen vacancy concentration” refers to the concentration of a special class of point defects of oxide materials, in which the lattice oxygen is missed from the bulk and two trapped electrons localizes in the cavity center.

[72] As used herein, “specific surface area” refers to a property of solids which is the total surface area of a material per unit of massy.

[73] As used herein, “oxygen storage capacity” refers to a value that allows for the evaluation of the ability of a material to store oxygen.

[74] As used herein, “specific surface Ce^{3+} ratio” refers to $n_{Ce3+}/(n_{Ce3+} + n_{Ce4+})$.

[75] As used herein, “noble metal” refers to a metal that is resistant to corrosion and oxidation in moist air. Noble metals include, but are not limited to, ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, mercury, and rhenium.

[76] As used herein, “metal oxide” refers to a chemical compound that contains at least one oxygen atom and at least one metal in its chemical formula.

[77] As used herein, “bi-metal” refers to a compound containing two distinct metals, including alloys.

[78] As used herein, “triple-metal” refers to a compound containing three distinct metals, including alloys.

[79] As used herein, “calcination” refers to a thermal treatment process in the presence of air or oxygen applied to a solid material to bring about a thermal decomposition, phase transition, or removal of a volatile fraction.

[80] 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 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.

CLAIMS

What is claimed is:

1. A method of making one or more porous CeO_2 nanoparticles, the method comprising: contacting $Ce(NO_3)_3$ and a base at a pressure and temperature to form a mixture; and converting the mixture into a composition comprising one or more porous CeO_2 nanoparticles.

2. A method of making one or more nanoparticles, the method comprising: contacting $Ce(NO_3)_3$ and a base at a pressure and temperature to form a mixture comprising the one or more nanoparticles.

3. The method of claim 2, further comprising converting the mixture into a composition comprising one or more porous CeO_2 nanoparticles.

4. The method of claim 2, wherein the base is NaOH, KOH, or combinations thereof.

5. The method of claim 2, wherein the base is NaOH.

6. The method of claim 2, wherein a ratio of $Ce(NO_3)_3$ to base is about 1:80 to about 1:200.

7. The method of claim 2, wherein a ratio of $Ce(NO_3)_3$ to base is about 1:120.

8. The method of claim 2, wherein the pressure is about 1.0 atmospheres to about 1.5 atmospheres.

9. The method of claim 2, wherein the temperature is about 100 °C.

10. The method of claim 2, wherein the temperature is 100 °C.

11. The method of claim 2, wherein the mixture comprises at least one of CeO_2 and $Ce(OH)_3$.

12. The method of claim 2, wherein the mixture comprises CeO_2 and $Ce(OH)_3$.

13. The method of claim 2, wherein the nanoparticles comprise a mixture of CeO_2 and $Ce(OH)_3$.

14. The method of claim 2, wherein the nanoparticles have an average length of about 40 nm to about 80 nm.

15. The method of claim 2, wherein the nanoparticles have an average diameter of about 5 nm to about 8 nm.

16. The method of claim 2, wherein the nanoparticles are rod-shaped.

17. The method of claim 2, wherein the nanoparticles are non-porous.

18. The method of claim 2, further comprising:

washing the mixture to remove excess base after contacting $Ce(NO_3)_3$ and the base.

19. The method of claim 18, wherein distilled water is used to wash the mixture.

20. The method of claim 18, wherein the washing results in the mixture having a neutral pH value.

21. The method of claim 2, further comprising dispersing the mixture in a liquid.

22. The method of claim 21, wherein the liquid comprises water.

23. The method of claim 21, wherein the liquid comprises a hydrophilic solvent.

24. The method of claim 21, wherein the liquid comprises an alcohol, a ketone, N-N-dimethylformamide, or combinations thereof.

25. The method of claim 3, wherein the mixture is converted into a composition comprising one or more porous CeO_2 nanoparticles by dehydrating the mixture.

26. The method of claim 25, wherein a hydrothermal method is used to dehydrate the mixture.

27. The method of claim 25, wherein the hydrothermal method uses an autoclave.

28. The method of claim 27, wherein the autoclave is set at a temperature of about 160 °C to about 200 °C.

29. The method of claim 27, wherein the autoclave is set at a temperature of about 160 °C.

30. The method of claim 27, wherein the mixture is in the autoclave for about 12 hours to about 24 hours.

31. The method of claim 27, wherein the mixture is in the autoclave for about 12 hours.

32. The method of claim 3, wherein the mixture is converted into a composition comprising one or more porous CeO_2 nanoparticles by calcination.

33. The method of claim 32, wherein the calcination occurs at a temperature of about 200 °C to about 600 °C.

34. The method of claim 32, wherein the calcination occurs at a temperature of about 300 °C.

35. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have an average length of about 40 nm to about 80 nm.

36. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have an average diameter of about 5 nm to about 8 nm.

37. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have one or more of high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, high specific surface Ce^{3+} ratio, or combinations thereof.

38. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have an oxygen vacancy concentration that is larger than the oxygen vacancy concentration of nonporous CeO_2 nanoparticles.

39. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have a specific surface area of at least about 95 m^2/g.

40. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have a specific surface area of about 95 m^2/g to about 150 m^2/g.

41. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have a specific surface area of about 141 m^2/g.

42. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have an oxygen storage capacity of at least about 700 μmol O_2/g.

43. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have an oxygen storage capacity of about 700 μmol O_2/g to about 900 μmol O_2/g.

44. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have an oxygen storage capacity of about 800 μmol O_2/g to about 900 μmol O_2/g.

45. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have an oxygen storage capacity of about 900 μmol O_2/g.

46. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have a specific surface Ce^{3+} ratio of at least about 9%.

47. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have a specific surface Ce^{3+} ratio of about 9% to about 33%.

48. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have a specific surface Ce^{3+} ratio of about 30.8%.

49. The method of claim 3, wherein the one or more porous CeO_2 nanoparticles have a specific surface Ce^{3+} ratio of about 33%.

50. The method of claim 3, further comprising dispersing at least one active component in the one or more porous CeO_2 nanoparticles.

51. The method of claim 50, wherein the at least one active component comprises at least one noble metal, at least one metal oxide, at least one bi-metal, at least one triple-metal, or combinations thereof.

52. The method of claim 51, wherein the at least one noble metal comprises ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, mercury, rhenium, silver, copper, or combinations thereof.

53. The method of claim 51, wherein the at least one metal oxide comprises CuO, NiO, Co_3O_4, or combinations thereof.

54. The method of claim 51, wherein the at least one bi-metal comprises PtPd, AuPd, or combinations thereof.

55. The method of claim 51, wherein the at least one bi-metal comprises two metals selected from Ni, Co, Au, Ag, Cu, Fe, Pt, Pd, Rh, Ru, and Ir.

56. The method of claim 51, wherein the at least one triple-metal comprises CoNiPt, CuPdAu, or combinations thereof.

57. The method of claim 51, wherein the at least one triple-metal comprises three metals selected from Ni, Co, Au, Ag, Cu, Fe, Pt, Pd, Rh, Ru, and Ir.

58. At least one porous CeO_2 nanoparticle having one or more of high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, high specific surface Ce^{3+} ratio, or combinations thereof.

59. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has an oxygen vacancy concentration that is larger than the oxygen vacancy concentration of nonporous CeO_2 nanoparticles.

60. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of at least about 95 m^2/g.

61. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of about 95 m^2/g to about 150 m^2/g.

62. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of about 141 m^2/g.

63. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of at least about 700 μmol O_2/g.

64. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 700 μmol O_2/g to about 900 μmol O_2/g.

65. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 800 μmol O_2/g to about 900 μmol O_2/g.

66. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 900 μmol O_2/g.

67. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of at least about 9%.

68. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 9% to about 33%.

69. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 30.8%.

70. The at least one porous CeO_2 nanoparticle of claim 58, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 33%.

71. The at least one porous CeO_2 nanoparticle of claim 58, further comprising at least one active component in the at least one porous CeO_2 nanoparticle.

72. The at least one porous CeO_2 nanoparticle of claim 71, wherein the at least one active component comprises at least one noble metal, at least one metal oxide, at least one bi-metal, at least one triple-metal, or combinations thereof.

73. The at least one porous CeO_2 nanoparticle of claim 72, wherein the at least one noble metal comprises ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, mercury, rhenium, silver, copper, or combinations thereof.

74. The at least one porous CeO_2 nanoparticle of claim 72, wherein the at least one metal oxide comprises CuO, NiO, Co_3O_4, or combinations thereof.

75. The at least one porous CeO_2 nanoparticle of claim 72, wherein the at least one bi-metal comprises PtPd, AuPd, or combinations thereof.

76. The at least one porous CeO_2 nanoparticle of claim 72, wherein the at least one bi-metal comprises two metals selected from Ni, Co, Au, Ag, Cu, Fe, Pt, Pd, Rh, Ru, and Ir.

77. The at least one porous CeO_2 nanoparticle of claim 72, wherein the at least one triple-metal comprises CoNiPt, CuPdAu, or combinations thereof.

78. The at least one porous CeO_2 nanoparticle of claim 72, wherein the at least one triple-metal comprises three metals selected from Ni, Co, Au, Ag, Cu, Fe, Pt, Pd, Rh, Ru, and Ir.

79. A catalyst system comprising:
at least one first catalyst; and
at least one co-catalyst, wherein the co-catalyst comprises at least one porous CeO_2 nanoparticle.

80. The catalyst system of claim 79, wherein the at least one first catalyst comprises CeO_2-ZrO_2, CeO_2-TiO_2, CeO_2-CdS, or combinations thereof.

81. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has one or more of high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, high specific surface Ce^{3+} ratio, or combinations thereof.

82. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has an oxygen vacancy concentration that is larger than the oxygen vacancy concentration of nonporous CeO_2 nanoparticles.

83. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of at least about 95 m^2/g.

84. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of about 95 m^2/g to about 150 m^2/g.

85. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of about 141 m^2/g.

86. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of at least about 700 μmol O_2/g.

87. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 700 μmol O_2/g to about 900 μmol O_2/g.

88. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 800 μmol O_2/g to about 900 μmol O_2/g.

89. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 900 μmol O_2/g.

90. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of at least about 9%.

91. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 9% to about 33%.

92. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 30.8%.

93. The catalyst system of claim 79, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 33%.

94. A catalyst system comprising:

a catalyst supported on a carrier, wherein the carrier comprises at least one porous CeO_2 nanoparticle.

95. The catalyst system of claim 94, wherein the catalyst comprises Pt, Au, Pd, Ni, Ru, NiO, CuO, or a combination thereof.

96. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has one or more of high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, high specific surface Ce^{3+} ratio, or combinations thereof.

97. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has an oxygen vacancy concentration that is larger than the oxygen vacancy concentration of nonporous CeO_2 nanoparticles.

98. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of at least about 95 m^2/g.

99. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of about 95 m^2/g to about 150 m^2/g.

100. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has a specific surface area of about 141 m^2/g.

101. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of at least about 700 μmol O_2/g.

102. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 700 μmol O_2/g to about 900 μmol O_2/g.

103. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 800 μmol O_2/g to about 900 μmol O_2/g.

104. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has an oxygen storage capacity of about 900 μmol O_2/g.

105. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of at least about 9%.

106. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 9% to about 33%.

107. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 30.8%.

108. The catalyst system of claim 94, wherein the at least one porous CeO_2 nanoparticle has a specific surface Ce^{3+} ratio of about 33%.

109. One or more nanoparticles prepared by a method comprising:

contacting $Ce(NO_3)_3$ and a base at a pressure and temperature to form a mixture comprising the one or more nanoparticles.

110. The one or more nanoparticles of claim 109, wherein the method further comprises converting the mixture into a composition comprising one or more porous CeO_2 nanoparticles.

111. The one or more nanoparticles of claim 109, wherein the base is NaOH, KOH, or combinations thereof.

112. The one or more nanoparticles of claim 109, wherein the base is NaOH.

113. The one or more nanoparticles of claim 109, wherein a ratio of $Ce(NO_3)_3$ to base is about 1:80 to about 1:200.

114. The one or more nanoparticles of claim 109, wherein a ratio of $Ce(NO_3)_3$ to base is about 1:120.

115. The one or more nanoparticles of claim 109, wherein the pressure is about 1.0 atmospheres to about 1.5 atmospheres.

116. The one or more nanoparticles of claim 109, wherein the temperature is about 100 °C.

117. The one or more nanoparticles of claim 109, wherein the temperature is 100 °C.

118. The one or more nanoparticles of claim 109, wherein the mixture comprises at least one of CeO_2 and $Ce(OH)_3$.

119. The one or more nanoparticles of claim 109, wherein the mixture comprises CeO_2 and $Ce(OH)_3$.

120. The one or more nanoparticles of claim 109, wherein the nanoparticles comprise a mixture of CeO_2 and $Ce(OH)_3$.

121. The one or more nanoparticles of claim 109, wherein the nanoparticles have an average length of about 40 nm to about 80 nm.

122. The one or more nanoparticles of claim 109, wherein the nanoparticles have an average diameter of about 5 nm to about 8 nm.

123. The one or more nanoparticles of claim 109, wherein the nanoparticles are rod-shaped.

124. The one or more nanoparticles of claim 109, wherein the nanoparticles are non-porous.

125. The one or more nanoparticles of claim 109, wherein the method further comprises: washing the mixture to remove excess base after contacting $Ce(NO_3)_3$ and the base.

126. The one or more nanoparticles of claim 125, wherein distilled water is used to wash the mixture.

127. The one or more nanoparticles of claim 125, wherein the washing results in the mixture having a neutral pH value.

128. The one or more nanoparticles of claim 109, wherein the method further comprises dispersing the mixture in a liquid.

129. The one or more nanoparticles of claim 128, wherein the liquid comprises water.

130. The one or more nanoparticles of claim 128, wherein the liquid comprises a hydrophilic solvent.

131. The one or more nanoparticles of claim 128, wherein the liquid comprises an alcohol, a ketone, N-N-dimethylformamide, or combinations thereof.

132. The one or more nanoparticles of claim 110, wherein the mixture is converted into a composition comprising one or more porous CeO_2 nanoparticles by dehydrating the mixture.

133. The one or more nanoparticles of claim 132, wherein a hydrothermal method is used to dehydrate the mixture.

134. The one or more nanoparticles of claim 132, wherein the hydrothermal method uses an autoclave.

135. The one or more nanoparticles of claim 132, wherein the autoclave is set at a temperature of about 160 °C to about 200 °C.

136. The one or more nanoparticles of claim 132, wherein the autoclave is set at a temperature of about 160 °C.

137. The one or more nanoparticles of claim 132, wherein the mixture is in the autoclave for about 12 hours to about 24 hours.

138. The one or more nanoparticles of claim 132, wherein the mixture is in the autoclave for about 12 hours.

139. The one or more nanoparticles of claim 110, wherein the mixture is converted into a composition comprising one or more porous CeO_2 nanoparticles by calcination.

140. The one or more nanoparticles of claim 139, wherein the calcination occurs at a temperature of about 200 °C to about 600 °C.

141. The one or more nanoparticles of claim 139, wherein the calcination occurs at a temperature of about 300 °C.

142. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have an average length of about 40 nm to about 80 nm.

143. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have an average diameter of about 5 nm to about 8 nm.

144. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have one or more of high oxygen vacancy concentration, high specific surface area, high oxygen storage capacity, high specific surface Ce^{3+} ratio, or combinations thereof.

145. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have an oxygen vacancy concentration that is larger than the oxygen vacancy concentration of nonporous CeO_2 nanoparticles.

146. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have a specific surface area of at least about 95 m^2/g.

147. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have a specific surface area of about 95 m^2/g to about 150 m^2/g.

148. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have a specific surface area of about 141 m^2/g.

149. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have an oxygen storage capacity of at least about 700 μmol O_2/g.

150. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have an oxygen storage capacity of about 700 μmol O_2/g to about 900 μmol O_2/g.

151. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have an oxygen storage capacity of about 800 μmol O_2/g to about 900 μmol O_2/g.

152. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have an oxygen storage capacity of about 900 μmol O_2/g.

153. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have a specific surface Ce^{3+} ratio of at least about 19%.

154. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have a specific surface Ce^{3+} ratio of about 19% to about 33%.

155. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have a specific surface Ce^{3+} ratio of about 30.8%.

156. The one or more nanoparticles of claim 110, wherein the one or more porous CeO_2 nanoparticles have a specific surface Ce^{3+} ratio of about 33%.

157. The one or more nanoparticles of claim 110, wherein the method further comprises dispersing at least one active component in the one or more porous CeO_2 nanoparticles.

158. The one or more nanoparticles of claim 157, wherein the at least one active component comprises at least one noble metal, at least one metal oxide, at least one bi-metal, at least one triple-metal, or combinations thereof.

159. The one or more nanoparticles of claim 158, wherein the at least one noble metal comprises ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, mercury, rhenium, or combinations thereof.

160. The one or more nanoparticles of claim 158, wherein the at least one metal oxide comprises CuO, NiO, Co_3O_4, or combinations thereof.

161. The one or more nanoparticles of claim 158, wherein the at least one bi-metal comprises PtPd, AuPd, or combinations thereof

162. The one or more nanoparticles of claim 158, wherein the at least one triple-metal comprises CoNiPt, CuPdAu, or combinations thereof.

Figure 1

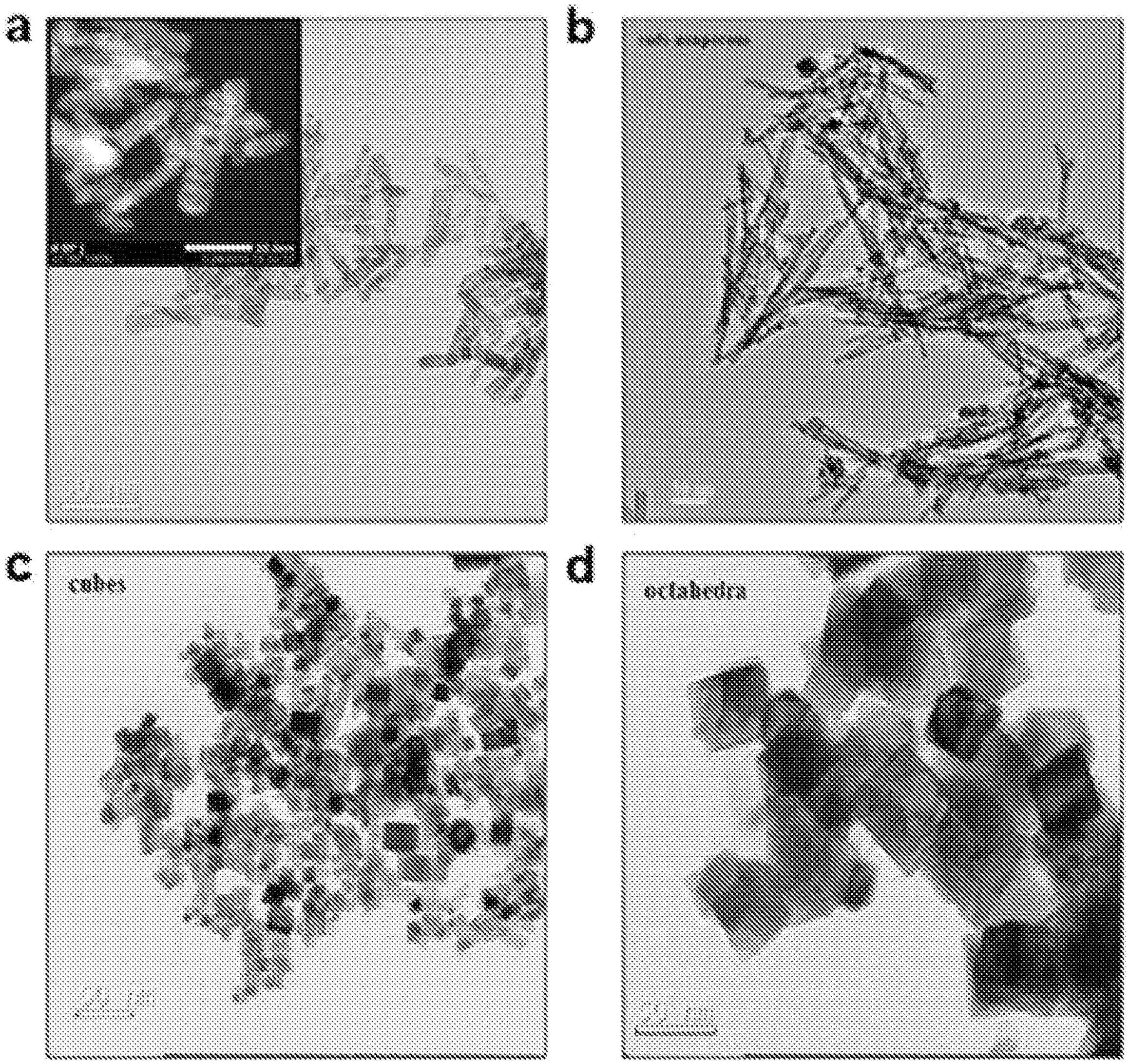

Figure 2

Sample	BET (m^2/g)	OSC (μmol O^2/g)	Ce^{3+} $3d_{5/2}$ in Ce (%)
porous-HY-120 °C	109	737.5	19.1
porous-HY-140 °C	120	864.3	24.3
porous-HY-160 °C	141	900	28.8
porous-HY-180 °C	131	831.7	33.0
porous-HY-200 °C	101	804.5	23.3
porous-Δ-200 °C	98	858	15.5
porous-Δ-300 °C	104	836.2	16.0
porous-Δ-400 °C	98	805.8	20.7
porous-Δ-500 °C	96	715.6	9.21

Figure 3

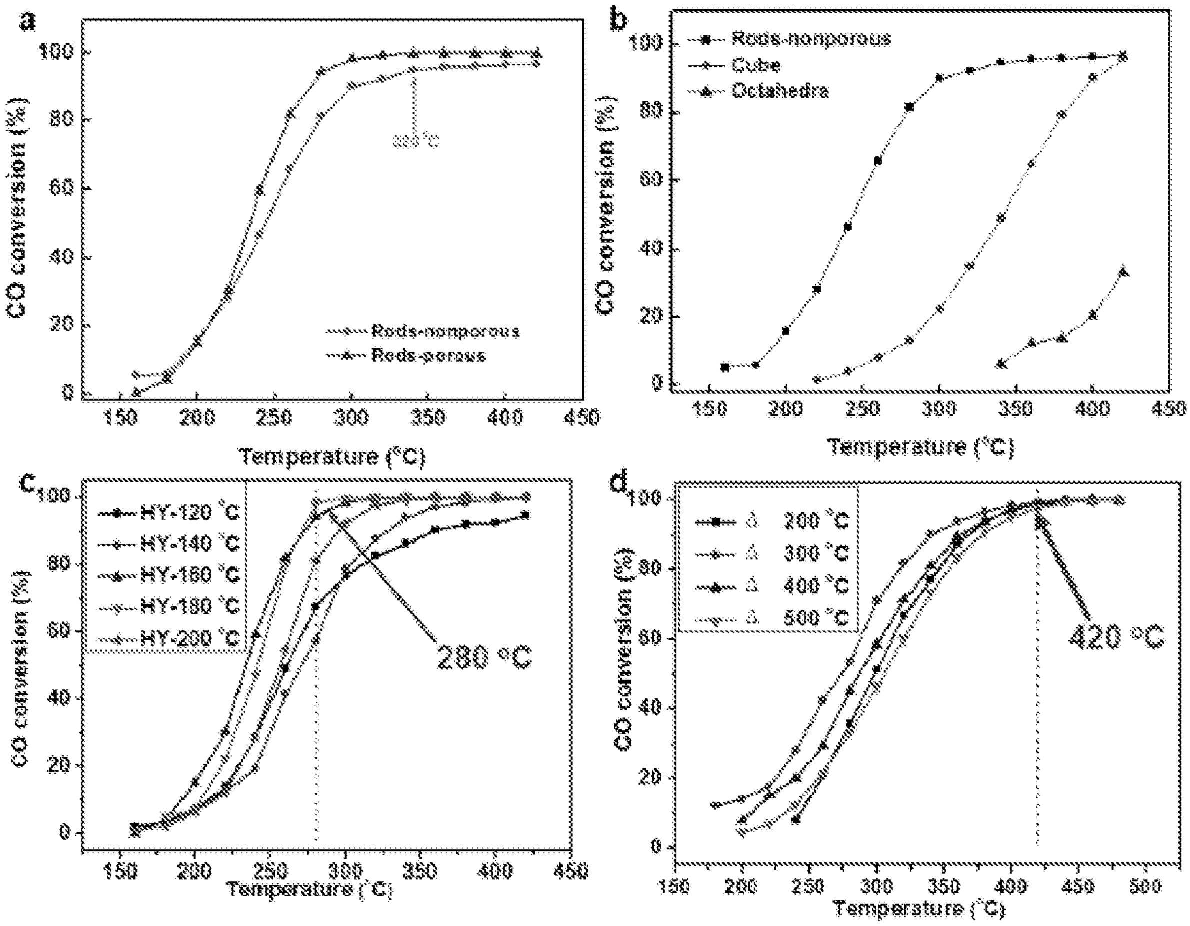
a
CO conversion (%)
0
20
40
60
80
100
150
200
250
300
350
400
450
Temperature (°C)
340 °C
Rods-nonporous
Rods-porous
b
CO conversion (%)
Rods-nonporous
Cube
Octahedra
Temperature (°C)
c
CO conversion (%)
HY-120 °C
HY-140 °C
HY-160 °C
HY-180 °C
HY-200 °C
280 °C
Temperature (°C)
d
CO conversion (%)
Δ 200 °C
Δ 300 °C
Δ 400 °C
Δ 500 °C
420 °C
500
Temperature (°C)

Figure 4

Sample	**BET (m^2/g)**	**OSC (µmol O_2/g)**
Porous CeO_2 nanorods	141	900
CeO_2 nanoplates	32	230.5
CeO_2 nanocrystals	61	357
CeO_2 particles	12	183
CeO_2 particles	93	258
CeO_2 nanorods	60.8	277
Mesoporous CeO_2	105	10
CeO_2-ZrO_2 particles	135	934
La-$Ce_{0.2}Zr_{0.8}O_2$ particles	144	363
Ni-$Ce_{0.67}Zr_{0.33}O_2$ particles	152	730

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/071872

A. CLASSIFICATION OF SUBJECT MATTER

B01J 37/00(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)

B01J37/- B01J23/-

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)

EPODOC;WPI;CNPAT;CNKI;CA:nanoparticle,porous,mixture,specific surface area,oxygen storage capacity,co-catalyst, catalyst system,catalyst carrier,temperature,pressure

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1792456 A (TIANJIN RES. & DESIGN INST. CHEM. IND.) 28 June 2006 (2006-06-28) Page 2 paragraph 3-page 3 paragraph 4， Page 4 paragraph 8	1-78，94-162
Y	CN 1792456 A (TIANJIN RES. & DESIGN INST. CHEM. IND.) 28 June 2006 (2006-06-28) Page 2 paragraph 3-page 3 paragraph 4， Page 4 paragraph 8	79-93
Y	CN 1546228 A (TIANJIN RES. & DESIGN INST. CHEM. IND.) 17 November 2004 (2004-11-17) Page 4 paragraph 4-page 6 paragraph 3	79-93

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

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"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

"&" document member of the same patent family

Date of the actual completion of the international search **14 October 2014**	Date of mailing of the international search report **14 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** Facsimile No. **(86-10)62019451**	Authorized officer **KONG,Deming** Telephone No. **(86-10)61648524**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2014/071872

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 1792456 A	28 June 2006	None	
CN 1546228 A	17 November 2004	CN 1264606 C	19 July 2006

Form PCT/ISA/210 (patent family annex) (July 2009)