

## **METHANATION CATALYST OF CARBON DIOXIDE, PREPARATION METHOD AND USAGE OF SAME**

### **FIELD OF THE INVENTION**

[0001] The invention relates to the catalytic synthesis technology, and more particularly to a catalyst for methanation of carbon dioxide, a preparation method and a usage thereof.

### **BACKGROUND OF THE INVENTION**

[0002] Currently, energy and environmental problems have become focuses of attention of the world. The first problem is that greenhouse effect resulted from the discharge of a large amount of greenhouse gases from the fossil energy and the consequent global warming have brought about comprehensive negative influence on respects of ecology, economy, and the social. With the global climate change, the global greenhouse effect has attracted more and more attention in the world. The large amount of CO<sub>2</sub> emission from the combustion of the fossil fuel is the primary reason causing the global climate change, and accounts for 60% of the contribution rate for the global warming. The second problem is that the insecurity factors of the clean energy, such as the nuclear energy, have brought about unprecedented challenges for the human production and survival.

[0003] How to effectively decrease the industrial discharge of CO<sub>2</sub> and transform CO<sub>2</sub> into a valuable resource is particularly important. The hydrogenation of CO<sub>2</sub> into CH<sub>4</sub> and fast methanation by catalysis are capable of realizing the resource utilization of CO<sub>2</sub>, as well as synthesizing new energies. Thus, the methanation reaction of catalytic hydrogenation of CO<sub>2</sub> has been one of the focuses in the carbon chemical research. In the study of the methanation reaction of catalytic hydrogenation of CO<sub>2</sub>, it is the key to select the catalyst possessing excellent performances, that is, low price, high activity, and high

reliability.

[0004] In conventional catalysts for methanation for carbon dioxide, most of them include alumina as the carrier and a single nickel or a nickel added with a single rare earth element as an active ingredient. Catalyst of this type has a relatively low catalytic activity and requires harsh reaction conditions, including relatively high pressure, low speed, and overdose of hydrogen, thereby resulting in high investment and low output. Publication No. CN1107078A has disclosed a catalyst for hydrogenation of carbon dioxide, the catalyst uses natural sepiolite as the carrier; however the natural sepiolite has very limited source, high production cost, thereby having no industrial applications. Publication No. CN1114955A has disclosed a catalyst for hydrogenation of carbon dioxide and a method for preparing the same, the catalyst therein is a nickel or ruthenium-based catalyst using special zirconium glue as the carrier. Publication No. CN101773833 has disclosed a catalyst for hydrogenation of carbon dioxide and a method for preparing the same, the catalyst therein is a nickel-based catalyst using oxide aerogels as the carrier. The above two catalysts have defects that the special zirconium glue or the oxide aerogels functions as the carrier is made of expensive nano-materials, thereby being difficult in application.

[0005] In another respect, the biomass power plant mainly generates electric power through the direct combustion of the agricultural and forestry waste. Since 2003, China has accelerated the pace for pushing the development of biomass power generation technology, and has identified the development goals of realizing an installed capacity of 30 million kilowatts of biomass power generation in 2020 in the published "long-term renewable energy development plan". As a promising renewable energy, the biomass power generation plays a very important role in treatment of agricultural and forestry solid wastes and abounding energy structure. With the continuous development of the biomass power industry, thorny issues were brought in, such as the difficulty in the combustion of the solid waste in the biomass power plant, and particularly the difficulty

in the resource utilization of ash (plant ash and rice husk ash) of the biomass power plant. In the ash from the biomass power plant, a primary composition is  $\text{SiO}_2$  and auxiliary compositions include  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$ , and a plurality of metal oxides have activation ability. Most of the ash from the biomass power plant has not been effectively utilized so far.

#### SUMMARY OF THE INVENTION

[0006] In view of the above-described problems, it is one objective of the invention to provide a catalyst for methanation of carbon dioxide, a method for preparing the same, and a method for using the same. The catalyst is prepared by using wasted ash from combustion of biomass as a carrier and using nickel as an active ingredient.

[0007] To achieve the above objective, there is provided a catalyst for methanation of carbon dioxide. The catalyst is formed by mixing ash from a biomass power plant with a nickel compound and calcining a resulting mixture. The catalyst formed by calcination comprises between 2 and 20 wt. % of nickel.

[0008] In the above technical solution, the nickel compound is selected from the group consisting of nickel nitrate, nickel oxalate, nickel formate, nickel acetate, nickel citrate, nickel tartrate, and a mixture thereof. The easily decomposable nickel compounds are capable of providing sufficient active ingredients for the carrier of the ash from the biomass power plant.

[0009] Preferably, the catalyst formed in the calcination comprises between 5 and 15 wt. % of nickel.

[0010] Preferably, the catalyst formed in the calcination comprises between 10 and 20 wt. % of nickel.

[0011] Preferably, the ash from the biomass power plant is selected from ash collected in

a bag dust collector. An average particle size of the ash from the biomass power plant is between 10 and 15  $\mu\text{m}$ , so that the active ingredients of nickel and the carrier of the ash from the biomass power plant are well fused in the calcination process.

[0012] A method for preparing the catalyst for methanation of carbon dioxide, the method comprises the following steps:

[0013] 1) preparing an aqueous solution comprising between 5 and 30 wt. % of the nickel compound;

[0014] 2) calcining the ash from the biomass power plant at a temperature of between 300 and 400°C for between 20 and 40 min for removing combustible impurities from the ash from the biomass power plant;

[0015] 3) calculating doses of raw materials according to a desired weight percent of nickel in a catalyst product, mixing the aqueous solution comprising the nickel compound with the ash from the biomass power plant after calcinations in step 2), and stirring a resulting mixture for between 5 and 10 h for uniformly impregnating the mixture;

[0016] 4) desiccating the ash from the biomass power plant after impregnation treatment at a temperature of between 110 and 150°C for between 0.5 and 1.5 h; and

[0017] 5) calcining the ash from the biomass power plant after desiccation treatment at a temperature of between 400 and 500°C for between 3 and 6 h to yield the catalyst for methanation of carbon dioxide.

[0018] Preferably, a calcination time in step 2) is controlled for between 25 and 30 min; a stirring time in step 3) is controlled for between 6 and 8 h; a desiccation time in step 4) is controlled for between 0.5 and 1.0 h; and a calcinations time in step 5) is controlled for between 4 and 5 h.

[0019] A method for using the catalyst for methanation of carbon dioxide is used in hydrogenation reaction of carbon dioxide in a fixed bed reactor. Specifically, activation

conditions of the catalyst are as follows: a particle size of the catalyst is between 40 and 60 meshes; a reaction pressure is normal pressure; a molar ratio between feed compositions is  $\text{H}_2/\text{CO}_2 = 4/1$ ; a volume space velocity is between 5500 and 9000  $\text{h}^{-1}$ ; a reaction temperature is between 250 and 450°C; and a reaction time is between 1 and 2 h.

[0020] Preferably, the activation conditions of the catalyst are as follows: the particle size of the catalyst is between 40 and 60 meshes; the reaction pressure is normal pressure; the molar ratio between feed compositions is  $\text{H}_2/\text{CO}_2 = 4/1$ ; the volume space velocity is between 6000 and 8000  $\text{h}^{-1}$ ; the reaction temperature is between 350 and 400°C; and the reaction time is 2 h.

[0021] Advantages of the invention are as follows: first, the catalyst carrier of the invention is directly selected from the ash from the biomass power plant, not only does it has a wide source and low cost, but also it changes waste into valuable and reaches the recycling of the waste, thereby solving the problem that the waste from the combustion in the biomass power plant is difficult to be treated. Second, the ash from the biomass power plant that is naturally mixed with a plurality of metals or metal oxides comprising a primary composition of  $\text{SiO}_2$  and auxiliary compositions comprising  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$ , so that as the catalyst carrier, the ash from the biomass power plant is not required to add with other additives. The content of the active ingredient of nickel in the carrier is controlled within 20 wt. %, and preferably between 10 and 20 wt. %, thereby largely decreasing the production cost. Third, the average particle size of the ash from the biomass power plant is controlled at between 10 and 15  $\mu\text{m}$ , the specific area is large, and the nickel or the compound thereof is loaded without mechanical crushing process, thereby further saving the production cost. Fourth, multi-metal oxide in the ash from the biomass power plant is capable of carrying nickel, enhancing the activity of the nickel on the  $\text{SiO}_2$  carrier, as well as regulating performances of the surface area, pore volume, and average pore radius of the carrier. Besides, the multi-metal oxide in the ash from the biomass power plant can be easily reduced and has excellent activity at low

temperature and low production cost.

[0022] In summary, the catalyst of the invention not only has relatively high catalytic activity and selectivity but also has a much higher stability; the catalyst is capable of effectively catalyzing the hydrogenation reaction of carbon dioxide in the normal pressure and facilitates the transformation of the carbon dioxide into the methane. The preparation method of the invention is capable of changing waste into valuable, and the operation thereof is simple. The cost of the preparation method from the source of the raw material to the manufacture of the production is very low, thereby being particularly suitable to the resource utilization of the ash from the biomass power plant.

#### DETAILED DESCRIPTION OF THE EMBODIMENTS

[0023] For further illustrating the invention, experiments detailing a catalyst for methanation of carbon dioxide, a preparation method and a usage thereof are described hereinbelow, but the content of the invention is not limited by the following examples.

##### **Example 1**

[0024] A method for preparing a catalyst comprising 5 wt. % of nickel for methanation of carbon dioxide (a content of nickel accounts for approximately 5 wt. % of a total weight of the catalyst, and remainders comprise ash from a biomass power plant and inevitable impurities).

[0025] 1) 1.441 g of nickel nitrate hexahydrate was added to a Bunsen beaker, deionized water was added to dissolve the nickel nitrate hexahydrate, a resulting solution was transferred to a 45 mL volumetric flask and calibrated to yield a nickel nitrate solution;

[0026] 2) ash from the biomass power plant was calcined at the temperature of 300°C for

40 min, and combustible impurities comprising  $\text{H}_2\text{O}$ , C, and  $\text{SO}_3$  were removed from the ash;

[0027] 3) 10 g of the ash from the biomass power plant after calcinations was added to an evaporating dish, 45 mL of the nickel nitrate solution was transferred from the volumetric flask to the evaporating dish for impregnating the mixture of biomass power plant, and a resulting mixture was stirred for 5 h;

[0028] 4) the ash from the biomass power plant after the impregnation treatment was desiccated at the temperature of  $120^\circ\text{C}$  for 1.0 h; and

[0029] 5) the ash from the biomass power plant after the desiccation was placed in a muffle furnace and then calcined at the temperature of  $450^\circ\text{C}$  for 5 h for decomposing salt therein, thereafter, the temperature was decreased to the room temperature, and the catalyst comprising 5 wt. % of nickel for methanation of carbon dioxide was yielded.

[0030] Application and analysis detection of the catalyst comprising 5 wt. % of nickel for methanation of carbon dioxide were as follows:

[0031] The catalyst comprising 5 wt. % of nickel for methanation of carbon dioxide was screened to obtain particles having a particle size of between 40 and 60 meshes. 1 g of the catalyst comprising 5 wt. % of nickel for methanation of carbon dioxide obtained from the screening treatment was placed in a fixed bed reactor. The fixed bed reactor was then heated to the temperature of  $400^\circ\text{C}$  and  $\text{H}_2$  having a flow of 100 mL/min was introduced for 1 h for reduction. After that, mixed reaction gases having a molar ratio of  $\text{H}_2/\text{CO}_2 = 4/1$  were introduced, and a product was analyzed and detected on line by gas chromatography under the following conditions: a reaction temperature of between  $250$  and  $450^\circ\text{C}$ , a reaction pressure of 0.1 MPa, a vacuum space velocity of between 5500 and  $9000\text{ h}^{-1}$ , and a circulating reaction time of 2 h. When the reaction temperature was  $400^\circ\text{C}$ , and the vacuum space velocity was  $6000\text{ h}^{-1}$ , a conversion rate of  $\text{CO}_2$  was 91.36 wt. %.

## Example 2

[0032] A method for preparing a catalyst comprising 10 wt. % of nickel for methanation of carbon dioxide (a content of nickel accounts for 10 wt. % of a total weight of the catalyst, and remainders comprise ash from a biomass power plant and inevitable impurities).

[0033] 1) 3.367 g of nickel nitrate hexahydrate was added to a Bunsen beaker, deionized water was added to dissolve the nickel nitrate hexahydrate, a resulting solution was transferred to a 45 mL volumetric flask and calibrated to yield a nickel nitrate solution;

[0034] 2) ash from a biomass power plant was calcined at the temperature of 350°C for 30 min, and combustible impurities comprising H<sub>2</sub>O, C, and SO<sub>3</sub> were removed from the ash;

[0035] 3) 10 g of the ash from the biomass power plant after calcinations was added to an evaporating dish, 45 mL of the nickel nitrate solution was transferred from the volumetric flask to the evaporating dish for impregnating the mixture of biomass power plant, and a resulting mixture was stirred for 6 h;

[0036] 4) the ash from the biomass power plant after the impregnation treatment was desiccated at the temperature of 150°C for 1.5 h; and

[0037] 5) the ash from the biomass power plant after the desiccation was placed in a muffle furnace and then calcined at the temperature of 450°C for 6 h for decomposing salt therein, thereafter, the temperature was decreased to the room temperature, and the catalyst comprising 10 wt. % of nickel for methanation of carbon dioxide was yielded.

[0038] Application and analysis detection of the catalyst comprising 10 wt. % of nickel for methanation of carbon dioxide were as follows:

[0039] The catalyst comprising 10 wt. % of nickel for methanation of carbon dioxide was screened to obtain particles having a particle size of between 40 and 60 meshes. 1 g of the catalyst comprising 10 wt. % of nickel for methanation of carbon dioxide obtained from the screening treatment was placed in a fixed bed reactor. The fixed bed reactor was then heated to the temperature of 400°C and H<sub>2</sub> having a flow of 100 mL/min was introduced for 1 h for reduction. After that, mixed reaction gases having a molar ratio of H<sub>2</sub>/CO<sub>2</sub> = 4/1 were introduced, and a product was analyzed and detected on line by gas chromatography under the following conditions: a reaction temperature of between 250 and 450°C, a reaction pressure of 0.1 MPa, a vacuum space velocity of between 5500 and 9000 h<sup>-1</sup>, and a circulating reaction time of 2 h. When the reaction temperature was 300°C, and the vacuum space velocity was 7000 h<sup>-1</sup>, a conversion rate of CO<sub>2</sub> was 95.21 wt. %.

### Example 3

[0040] A method for preparing a catalyst comprising 15 wt. % of nickel for methanation of carbon dioxide (a content of nickel accounts for 15 wt. % of a total weight of the catalyst, and remainders comprise ash from a biomass power plant and inevitable impurities).

[0041] 1) 6.073 g of nickel nitrate hexahydrate was added to a Bunsen beaker, deionized water was added to dissolve the nickel nitrate hexahydrate, a resulting solution was transferred to a 45 mL volumetric flask and calibrated to yield a nickel nitrate solution;

[0042] 2) ash from a biomass power plant was calcined at the temperature of 350°C for 30 min, and combustible impurities comprising H<sub>2</sub>O, C, and SO<sub>3</sub> were removed from the ash;

[0043] 3) 10 g of the ash from the biomass power plant after calcinations was added to an evaporating dish, 45 mL of the nickel nitrate solution was transferred from the volumetric

flask to the evaporating dish for impregnating the mixture of biomass power plant, and a resulting mixture was stirred for 7 h;

[0044] 4) the ash from the biomass power plant after the impregnation treatment was desiccated at the temperature of 150°C for 0.5 h; and

[0045] 5) the ash from the biomass power plant after the desiccation was placed in a muffle furnace and then calcined at the temperature of 450°C for 4 h for decomposing salt therein, thereafter, the temperature was decreased to the room temperature, and the catalyst comprising 15 wt. % of nickel for methanation of carbon dioxide was yielded.

[0046] Application and analysis detection of the catalyst comprising 15 wt. % of nickel for methanation of carbon dioxide were as follows:

[0047] The catalyst comprising 15 wt. % of nickel for methanation of carbon dioxide was screened to obtain particles having a particle size of between 40 and 60 meshes. 1 g of the catalyst comprising 15 wt. % of nickel for methanation of carbon dioxide obtained from the screening treatment was placed in a fixed bed reactor. The fixed bed reactor was then heated to the temperature of 400°C and H<sub>2</sub> having a flow of 100 mL/min was introduced for 1 h for reduction. After that, mixed reaction gases having a molar ratio of H<sub>2</sub>/CO<sub>2</sub> = 4/1 were introduced, and a product was analyzed and detected on line by gas chromatography under the following conditions: a reaction temperature of between 250 and 450°C, a reaction pressure of 0.1 MPa, a vacuum space velocity of between 5500 and 9000 h<sup>-1</sup>, and a circulating reaction time of 2 h. When the reaction temperature was 400°C, and the vacuum space velocity was 7000 h<sup>-1</sup>, a conversion rate of CO<sub>2</sub> was 97.87 wt. %.

#### **Example 4**

[0048] A method for preparing a catalyst comprising 20 wt. % of nickel for methanation of carbon dioxide (a content of nickel accounts for 20 wt. % of a total weight of the

catalyst, and remainders comprise ash from a biomass power plant and inevitable impurities).

[0049] 1) 10.152 g of nickel nitrate hexahydrate was added to a Bunsen beaker, deionized water was added to dissolve the nickel nitrate hexahydrate, a resulting solution was transferred to a 45 mL volumetric flask and calibrated to yield a nickel nitrate solution;

[0050] 2) ash from a biomass power plant was calcined at the temperature of 400°C for 20 min, and combustible impurities comprising H<sub>2</sub>O, C, and SO<sub>3</sub> were removed from the ash;

[0051] 3) 10 g of the ash from the biomass power plant after calcinations was added to an evaporating dish, 45 mL of the nickel nitrate solution was transferred from the volumetric flask to the evaporating dish for impregnating the mixture of biomass power plant, and a resulting mixture was stirred for 8 h;

[0052] 4) the ash from the biomass power plant after the impregnation treatment was desiccated at the temperature of 150°C for 1.0 h; and

[0053] 5) the ash from the biomass power plant after the desiccation was placed in a muffle furnace and then calcined at the temperature of 450°C for 3 h for decomposing salt therein, thereafter, the temperature was decreased to the room temperature, and the catalyst comprising 20 wt. % of nickel for methanation of carbon dioxide was yielded.

[0054] Application and analysis detection of the catalyst comprising 20 wt. % of nickel for methanation of carbon dioxide were as follows:

[0055] The catalyst comprising 20 wt. % of nickel for methanation of carbon dioxide was screened to obtain particles having a particle size of between 40 and 60 meshes. 1 g of the catalyst comprising 20 wt. % of nickel for methanation of carbon dioxide obtained from the screening treatment was placed in a fixed bed reactor. The fixed bed reactor was then heated to the temperature of 400°C and H<sub>2</sub> having a flow of 100 mL/min was introduced

for 1 h for reduction. After that, mixed reaction gases having a molar ratio of  $\text{H}_2/\text{CO}_2 = 4/1$  were introduced, and a product was analyzed and detected on line by gas chromatography under the following conditions: a reaction temperature of between 250 and 450°C, a reaction pressure of 0.1 MPa, a vacuum space velocity of between 5500 and 9000  $\text{h}^{-1}$ , and a circulating reaction time of 2 h. When the reaction temperature was 400°C, and the vacuum space velocity was 6000  $\text{h}^{-1}$ , a conversion rate of  $\text{CO}_2$  was 96.91 wt. %.

## CLAIMS

1. A catalyst for methanation of carbon dioxide, the catalyst being formed by mixing ash from a biomass power plant with a nickel compound and calcining a resulting mixture, and the catalyst formed by calcination comprising between 2 and 20 wt. % of nickel;

wherein the catalyst for methanation of carbon dioxide is prepared by a method, the method comprising the following steps:

- 1) preparing an aqueous solution comprising between 5 and 30 wt. % of the nickel compound;
- 2) calcining the ash from the biomass power plant at a temperature of between 300 and 400°C for between 20 and 40 min for removing combustible impurities from the ash from the biomass power plant;
- 3) calculating doses of raw materials according to a desired weight percent of nickel in a catalyst product, mixing the aqueous solution comprising the nickel compound with the ash from the biomass power plant after calcinations in step 2), and stirring a resulting mixture for between 5 and 10 h for uniformly impregnating the mixture;
- 4) desiccating the ash from the biomass power plant after impregnation treatment at a temperature of between 110 and 150°C for between 0.5 and 1.5 h; and
- 5) calcining the ash from the biomass power plant after desiccation treatment at a temperature of between 400 and 450°C for between 3 and 6 h and being screened to obtain particles having a particle size of between 40 and 60 meshes to yield the catalyst for methanation of carbon dioxide.

2. The catalyst of claim 1, **characterized in that** the catalyst formed in the calcination comprises between 5 and 15 wt. % of nickel.
3. The catalyst of claim 1, **characterized in that** the catalyst formed in the calcination comprises between 10 and 20 wt. % of nickel.
4. The catalyst of any one of claims 1-3, **characterized in that** the nickel compound is selected from the group consisting of nickel nitrate, nickel oxalate, nickel formate, nickel acetate, nickel citrate, nickel tartrate, and a mixture thereof.
5. The catalyst of any one of claims 1-3, **characterized in that** the ash from the biomass power plant is selected from ash collected in a bag dust collector and has an average particle size of between 10 and 15  $\mu\text{m}$ .
6. The catalyst of claim 4, **characterized in that** an average particle size of the ash from the biomass power plant is between 10 and 15  $\mu\text{m}$ .
7. The catalyst of claim 1, **characterized in that**
  - a calcination time in step 2) is controlled for between 25 and 30 min;
  - a stirring time in step 3) is controlled for between 6 and 8 h;
  - a desiccation time in step 4) is controlled for between 0.5 and 1.0 h; and
  - a calcinations time in step 5) is controlled for between 4 and 5 h.

8. A method for using the catalyst for methanation of carbon dioxide of claim 1 for a hydrogenation reaction of carbon dioxide in a fixed bed reactor, **characterized in that** activation conditions of the catalyst are as follows:

a particle size of the catalyst is between 40 and 60 meshes;

a reaction pressure is normal pressure;

a molar ratio between feed compositions is  $H_2/CO_2 = 4/1$ ;

a volume space velocity is between 5500 and 9000  $h^{-1}$ ;

a reaction temperature is between 250 and 450°C; and

a reaction time is between 1 and 2 h.

9. The method of claim 8, **characterized in that** the activation conditions of the catalyst are as follows:

the particle size of the catalyst is between 40 and 60 meshes;

the reaction pressure is normal pressure;

the molar ratio between feed compositions is  $H_2/CO_2 = 4/1$ ;

the volume space velocity is between 6000 and 8000  $h^{-1}$ ;

the reaction temperature is between 350 and 400°C; and

the reaction time is 2 h.