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(54) Title: NICKEL OXIDE PARTICLES AND METHOD FOR PRODUCING THE SAME

(57) Abstract: Nickel oxide particles contain molybdenum. In the nickel oxide particles, the molybdenum may be unevenly distributed in a surface layer of the nickel oxide particles. A crystallite diameter of a [100] plane of the nickel oxide particles may be 240 nm or more. A crystallite diameter of a [101] plane of the nickel oxide particles may be 220 nm or more. A median diameter D_{50} of the nickel oxide particles calculated by a laser diffraction/scattering method may be 10.00 μm or more and 1000.00 μm or less. A method for producing the nickel oxide particles includes calcining a nickel compound in presence of a molybdenum compound. The molybdenum compound may be at least one compound selected from a group including molybdenum trioxide, lithium molybdate, potassium molybdate and sodium molybdate. In the method for producing the nickel oxide particles, a calcination temperature may be 800°C or higher and 1600°C or lower.

DESCRIPTION

TITLE OF INVENTION: NICKEL OXIDE PARTICLES AND METHOD FOR PRODUCING THE SAME

TECHNICAL FIELD

[0001]

The present invention relates to nickel oxide particles and a method for producing the nickel oxide particles.

BACKGROUND ART

[0002]

Nickel oxide powders are used for various applications such as materials for electronic parts and materials for batteries, and some of them are reduced to nickel powders and then used as materials for conductive fillers and the materials for batteries.

[0003]

Generally, the nickel oxide powders are produced by calcining, in an oxidizing atmosphere, a nickel salt such as nickel sulfate, nickel nitrate, nickel carbonate, or nickel hydroxide, or nickel metal powders using a rolling furnace such as a rotary kiln, a continuous furnace such as a pusher furnace, or a batch furnace such as a burner furnace. For example, PTL 1 discloses a method for producing the nickel oxide powders by obtaining the nickel oxide powders having a sulfur grade of 500 ppm or less using anhydrous nickel sulfate as a raw material by roasting at a maximum temperature of 900 to 1200°C using a horizontal rotary production furnace while forcibly flowing air into the furnace from an outlet side to an inlet side at a flow rate of 15 mm/sec or more with respect to a cross-sectional area of the furnace.

Citation List

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Patent Literature

[0004]

PTL 1: JP-A-2004-189530

SUMMARY OF INVENTION

Technical Problem

[0005]

However, nickel oxide obtained by the method of PTL 1 or the like tends to be fine primary particles having an average particle diameter of 5.0 μm or less and secondary aggregates thereof.

[0006]

The present invention has been made in view of the above circumstances, and provides the nickel oxide particles having a controlled particle diameter and particle size distribution, and a method for producing the nickel oxide particles.

Solution to Problem

[0007]

That is, the present invention includes the following aspects.

(1) Nickel oxide particles containing molybdenum.

(2) The nickel oxide particles according to (1) above, in which the molybdenum is unevenly distributed in a surface layer of the nickel oxide particles.

(3) The nickel oxide particles according to (1) or (2) above, in which a crystallite diameter of a [100] plane of the nickel oxide particles is 240 nm or more.

(4) The nickel oxide particles according to any one of (1) to (3) above, in which a crystallite diameter of a [101] plane of the nickel oxide particles is 220 nm or more.

(5) The nickel oxide particles according to any one of (1) to (4) above, in which a median diameter D_{50} of the nickel oxide particles calculated by a laser diffraction/scattering method is 10.00 μm or more and 1000.00 μm or less.

(6) The nickel oxide particles according to any one of (1) to (5) above, in which

NiO content N_1 with respect to 100 mass% of the nickel oxide particles determined by

XRF analysis of the nickel oxide particles is 60.00 mass% or more and 99.60 mass% or less, and

MoO_3 content M_1 with respect to 100 mass% of the nickel oxide particles determined by XRF analysis of the nickel oxide particles is 0.04 mass% or more and 40.00 mass% or less.

(7) The nickel oxide particles according to any one of (1) to (6) above, in which

NiO content N_2 with respect to 100 mass% of a surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles is 10.00 mass% or more and 70.00 mass% or less, and

MoO_3 content M_2 with respect to 100 mass% of the surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles is 20.00 mass% or more and 40.00 mass% or less.

(8) The nickel oxide particles according to any one of (1) to (7) above, in which a surface layer uneven distribution ratio M_2/M_1 of MoO_3 content M_2 with respect to 100 mass% of a surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles to MoO_3 content M_1 with respect to 100 mass% of the nickel oxide particles determined by XRF analysis of the nickel oxide particles is 0.05 or more and 1000.00 or less.

(9) A method for producing the nickel oxide particles according to any one of (1) to (8) above, including calcining a nickel compound in presence of a molybdenum compound.

(10) The method for producing the nickel oxide particles according to (9) above, in which the molybdenum compound is at least one compound selected from a group including molybdenum trioxide, lithium molybdate, potassium molybdate and sodium molybdate.

(11) The method for producing the nickel oxide particles according to (9) or (10) above, in which a calcination temperature is 800°C or higher and 1600°C or lower.

Advantageous Effects of Invention

[0008]

According to the nickel oxide particles of the above aspects and the method for producing the nickel oxide particles, the nickel oxide particles having a controlled particle diameter and particle size distribution can be obtained.

BRIEF DESCRIPTION OF DRAWINGS

[0009]

Fig. 1 is a scanning electron microscope (SEM) image of nickel oxide particles of Example 1. A scale bar is 50.0 μm.

Fig. 2 is an SEM image of the nickel oxide particles of Example 2. Scale bars are respectively 5.00 μm (left side) and 1.00 μm (right side).

Fig. 3 is an SEM image of the nickel oxide particles of Comparative Example 1. The scale bar is 5.00 μm.

Fig. 4 is an SEM image of the nickel oxide particles of Comparative Example 2. The scale bar is 5.00 μm.

Fig. 5 is a graph illustrating measurement results of the nickel oxide particles of Examples and Comparative Examples by an X-ray diffraction method (XRD method).

DESCRIPTION OF EMBODIMENTS

[0010]

Hereinafter, an embodiment of nickel oxide particles and a method for producing the nickel oxide particles of the present invention will be described.

[0011]

<<Nickel oxide particles>>

The nickel oxide particles of the embodiment contain molybdenum. The nickel oxide particles of the embodiment contain molybdenum and have excellent properties such as catalytic activity derived from molybdenum.

[0012]

In the nickel oxide particles of the embodiment, the molybdenum is preferably unevenly distributed in a surface layer of the nickel oxide particles.

Here, the "surface layer" in this specification means within 10 nm from a surface of the nickel oxide particles of the embodiment. This distance corresponds to a detection depth of XPS used for measurement in Examples.

Here, "unevenly distributed in the surface layer" means that a mass of molybdenum or the molybdenum compound per unit volume in the surface layer is greater than that of molybdenum or the molybdenum compound per unit volume other than the surface layer.

[0013]

In the nickel oxide particles of the embodiment, the fact that molybdenum is unevenly distributed in the surface layer of the nickel oxide particles is confirmed by the fact that MoO_3 content (M_2) with respect to 100 mass% of the surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles is greater than MoO_3 content (M_1) with respect to 100 mass% of the surface layer of the nickel oxide particles determined by XRF (fluorescent X-ray) analysis of the nickel oxide particles as described in Examples described below.

[0014]

In the nickel oxide particles of the embodiment, as an index that molybdenum is unevenly distributed in the surface layer of the nickel oxide particles, a surface layer uneven distribution ratio (M_2/M_1) of the MoO_3 content (M_2) to the MoO_3 content (M_1) of the nickel oxide particles of the embodiment is preferably 0.05 or more and 1000.00 or less, more preferably 1.00 or more and 700.00 or less, and even more preferably 20.00 or more and 600.00 or less.

[0015]

By unevenly distributing molybdenum or the molybdenum compound in the surface layer, excellent properties such as catalytic activity can be efficiently imparted as compared with a case where molybdenum or the molybdenum compound is uniformly present not only in the surface layer but also in other than the surface layer (inner layer).

[0016]

The nickel oxide particles of the embodiment produced by a production method of the embodiment can have a unique granular (spherical) shape as described in Examples described below.

[0017]

In the nickel oxide particles of the embodiment, a particle size and molybdenum content of nickel oxide particles obtained can be controlled by controlling a used amount and type of the molybdenum compound in the production method described below.

[0018]

In the nickel oxide particles of the embodiment, a crystallite diameter of a [100] plane is preferably 240 nm or more, more preferably 250 nm or more, even more preferably 260 nm or more, and particularly preferably 290 nm or more. In the nickel oxide particles of the embodiment, the crystallite diameter of the [100] plane may be 1000 nm or less, 900 nm or less,

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or 800 nm or less.

[0019]

In this specification, as the crystallite diameter of the [100] plane of the nickel oxide particles, a value of the crystallite diameter calculated by using Scherrer equation from a half width of a peak (that is, a peak appearing near $2\theta = 37.3°$) attributed to the [100] plane measured by an X-ray diffraction method (XRD method) shall be adopted.

[0020]

In the nickel oxide particles of the embodiment, a crystallite diameter of a [101] plane is preferably 220 nm or more, more preferably 250 nm or more, even more preferably 290 nm or more, and particularly preferably 310 nm or more. In the nickel oxide particles of the embodiment, the crystallite diameter of the [101] plane may be 700 nm or less, 500 nm or less, or 400 nm or less.

[0021]

In this specification, as the crystallite diameter of the [101] plane of the nickel oxide particles, a value of the crystallite diameter calculated by using the Scherrer equation from a half width of a peak (that is, a peak appearing near $2\theta = 43.3°$) attributed to the [101] plane measured by the X-ray diffraction method (XRD method) shall be adopted.

[0022]

As an example of the nickel oxide particles of the embodiment, the nickel oxide particles having a crystallite diameter of the [100] plane of 240 nm or more and a crystallite diameter of the [101] plane of 220 nm or more can be exemplified. The nickel oxide particles can be more crystalline.

[0023]

A median diameter D_{50} of the nickel oxide particles of the embodiment calculated by a laser diffraction/scattering method is preferably 10.00 μm or more and 1000.00 μm or less, more preferably 11.00 μm or more and 100.00 μm or less, even more preferably 12.00 μm or more and 70.00 μm or less, and particularly preferably 13.00 μm or more and 65.00 μm or less.

[0024]

The median diameter D_{50} of the nickel oxide particles calculated by the laser diffraction/scattering method can be determined as a particle diameter in which a ratio of cumulative volume% is 50% in a particle diameter distribution measured by a dry method using a laser diffraction type particle size distribution meter.

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[0025]

A particle diameter D_{10} of the nickel oxide particles of the embodiment calculated by the laser diffraction/scattering method is preferably 3.00 μm or more and 100.00 μm or less, more preferably 5.00 μm or more and 50.00 μm or less, and even more preferably 6.00 μm or more and 40.00 μm or less.

[0026]

The particle diameter D_{10} of the nickel oxide particles calculated by the laser diffraction/scattering method can be determined as a particle diameter in which the ratio of cumulative volume% from a small particle side is 10% in the particle diameter distribution measured by the dry method using the laser diffraction type particle size distribution meter.

[0027]

A particle diameter D_{90} of the nickel oxide particles of the embodiment calculated by the laser diffraction/scattering method is preferably 13.00 μm or more and 1500.00 μm or less, more preferably 20.00 μm or more and 300.00 μm or less, and even more preferably 30.00 μm or more and 100.00 μm or less.

[0028]

The particle diameter D_{90} of the nickel oxide particles calculated by the laser diffraction/scattering method can be determined as a particle diameter in which the ratio of cumulative volume% from the small particle side is 90% in the particle diameter distribution measured by the dry method using the laser diffraction type particle size distribution meter.

[0029]

The nickel oxide particles of the embodiment contain nickel oxide. Examples of nickel oxide that the nickel oxide particles of the embodiment may contain include NiO.

[0030]

Nickel oxide content in the nickel oxide particles can be measured by XRF analysis. In the nickel oxide particles of the embodiment, NiO content N_1 with respect to 100 mass% of the nickel oxide particles determined by XRF analysis of the nickel oxide particles is preferably 60.00 mass% or more and 99.60 mass% or less, more preferably 90.00 mass% or more and 99.60 mass% or less, and even more preferably 95.00 mass% or more and 99.60 mass% or less.

[0031]

The nickel oxide particles of the embodiment contain molybdenum. In the nickel oxide particles of the embodiment, MoO_3 content M_1 with respect to 100 mass% of the nickel

oxide particles determined by XRF analysis of the nickel oxide particles is preferably 0.04 mass% or more and 40.00 mass% or less, more preferably 0.04 mass% or more and 20.00 mass% or less, even more preferably 0.04 mass% or more and 10.00 mass% or less, and particularly preferably 0.04 mass% or more and 1.50 mass% or less.

[0032]

Upper limit values and lower limit values of the NiO content N_1 and the MoO_3 content M_1 exemplified above in the nickel oxide particles of the embodiment can be freely combined. Further, numerical values of the NiO content N_1 and the MoO_3 content M_1 can be freely combined.

[0033]

As an example of the nickel oxide particles of the embodiment, the nickel oxide particles having the NiO content N_1 of 60.00 mass% or more and 99.60 mass% or less, and the MoO_3 content M_1 of 0.04 mass% or more and 40.00 mass% or less can be exemplified.

[0034]

The NiO content N_1 and the MoO_3 content M_1 can be measured by XRF analysis, for example, using a fluorescent X-ray analyzer (PrimusIV) manufactured by Rigaku Corporation.

[0035]

The nickel oxide content contained in the surface layer of the nickel oxide particles can be measured by X-ray photoelectron spectroscopy (XPS) surface analysis. In the nickel oxide particles of the embodiment, NiO content N_2 with respect to 100 mass% of the surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles is preferably 10.00 mass% or more and 70.00 mass% or less, more preferably 30.00 mass% or more and 60.00 mass% or less, and even more preferably 50.00 mass% or more and 55.00 mass% or less.

[0036]

In the nickel oxide particles of the embodiment, MoO_3 content M_2 with respect to 100 mass% of the surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles is preferably 2.00 mass% or more and 40.00 mass% or less, more preferably 10.00 mass% or more and 37.00 mass% or less, and even more preferably 25.00 mass% or more and 35.00 mass% or less.

[0037]

Upper limit values and lower limit values of the NiO content N_2 and the MoO_3 content

M_2 exemplified above in the nickel oxide particles of the embodiment can be freely combined. Further, numerical values of the NiO content N_2 and the MoO_3 content M_2 can be freely combined.

[0038]

As an example of the nickel oxide particles of the embodiment, the nickel oxide particles having the NiO content N_2 of 10.00 mass% or more and 70.00 mass% or less, and the MoO_3 content M_2 of 20.00 mass% or more and 40.00 mass% or less can be exemplified.

[0039]

The above NiO content N_2 refers to a value determined as the content of NiO with respect to 100 mass% of the surface layer of the nickel oxide particles by obtaining an abundance ratio (atom%) for each element by XPS surface analysis of the nickel oxide particles by X-ray photoelectron spectroscopy (XPS) and by converting the nickel content to oxide.

[0040]

The above MoO_3 content M_2 refers to a value determined as the content of MoO_3 with respect to 100 mass% of the surface layer of the nickel oxide particles by obtaining an abundance ratio (atom%) for each element by XPS surface analysis of the nickel oxide particles by X-ray photoelectron spectroscopy (XPS) and by converting the molybdenum content to oxide.

[0041]

The nickel oxide particles of the embodiment may further contain lithium, potassium, or sodium in addition to molybdenum.

[0042]

<Method for producing nickel oxide particles>

The method for producing the nickel oxide particles of the embodiment (hereinafter, simply referred to as the "production method of the embodiment") includes a step of calcining a nickel compound in presence of the molybdenum compound. More specifically, the production method of the embodiment is the method for producing the nickel oxide particles, which may include mixing the nickel compound and the molybdenum compound to form a mixture, and calcining the mixture.

[0043]

According to the method for producing the nickel oxide particles of the embodiment, the nickel oxide particles of the embodiment described above can be produced.

[0044]

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A preferred method for producing the nickel oxide particles includes a step (mixing step) of mixing the nickel compound and the molybdenum compound to form the mixture, and a step (calcination step) of calcining the mixture.

[0045]

[Mixing step]

The mixing step is a step of mixing the nickel compound and the molybdenum compound to form the mixture. The contents of the mixture will be described below.

[0046]

(Nickel compound)

The nickel compound is not limited as long as it is a compound that can be calcined to the nickel oxide. Examples of the nickel compound include the nickel oxide, nickel hydroxide, nickel oxyhydroxide, nickel sulfate, nickel nitrate, nickel carbonate and the like, and the nickel oxide is preferable. The nickel oxide may be NiO (nickel oxide (II)), Ni_2O_3 (nickel oxide (III)), NiO_2 (nickel oxide (IV)), NiO, or nickel oxide containing one or more selected from a group including Ni_2O_3 and NiO_2.

[0047]

Since a shape of the nickel oxide particles after calcination hardly reflects a shape of a raw material nickel compound, any shape such as a sphere, an amorphous shape, a structure having an aspect (a wire, a fiber, a ribbon, a tube, or the like), or a sheet can be suitably used as the nickel compound.

[0048]

(Molybdenum compound)

Examples of the molybdenum compound include molybdenum oxide and molybdate compounds.

[0049]

Examples of the molybdenum oxide include molybdenum dioxide and molybdenum trioxide, and the molybdenum trioxide is preferable.

[0050]

The molybdate compound is not limited as long as it is a salt compound of molybdenum oxoanion such as MoO_4^{2-}, $Mo_2O_7^{2-}$, $Mo_3O_{10}^{2-}$, $Mo_4O_{13}^{2-}$, $Mo_5O_{16}^{2-}$, $Mo_6O_{19}^{2-}$, $Mo_7O_{24}^{6-}$, or $Mo_8O_{26}^{4-}$. It may be an alkali metal salt of the molybdenum oxoanion, an alkaline earth metal salt, or an ammonium salt.

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[0051]

As the molybdate compound, the alkali metal salt of the molybdenum oxoanion is preferable, lithium molybdate, potassium molybdate or sodium molybdate is more preferable, and potassium molybdate or sodium molybdate is further preferable.

[0052]

In the production method of the embodiment, the molybdate compound may be a hydrate.

[0053]

The molybdate compound is preferably at least one compound selected from a group including molybdenum trioxide, lithium molybdate, potassium molybdate, and sodium molybdate, and more preferably at least one compound selected from a group including molybdenum trioxide, potassium molybdate, and sodium molybdate.

[0054]

The production method of the embodiment may include a step of calcining the nickel compound in the presence of the molybdenum compound and a potassium compound.

[0055]

The production method of the embodiment can include the step (mixing step) of mixing the nickel compound, the molybdenum compound, and the potassium compound to form the mixture prior to the calcination step, and can include the step (calcination step) of calcining the mixture.

[0056]

Alternatively, the production method of the embodiment can include the step (mixing step) of mixing the nickel compound and a compound containing molybdenum and potassium to form the mixture prior to the calcination step, and can include the step (calcination step) of calcining the mixture.

[0057]

The compound containing molybdenum and potassium, which is suitable as a flux agent, can be produced, for example, using a molybdenum compound and a potassium compound, which are cheaper and more easily available, as raw materials in the calcination step. Here, both when the molybdenum compound and the potassium compound are used as the flux agent and when the compound containing molybdenum and potassium is used as the flux agent are combined and regarded as when the molybdenum compound and the potassium compound are

used as the flux agent, that is, in the presence of the molybdenum compound and the potassium compound.

[0058]

The production method of the embodiment may include a step of calcining the nickel compound in the presence of the molybdenum compound and a sodium compound.

[0059]

The production method of the embodiment can include a step (mixing step) of mixing the nickel compound, the molybdenum compound, and the sodium compound to form the mixture prior to the calcination step, and can include a step (calcination step) of calcining the mixture.

[0060]

Alternatively, the production method of the embodiment can include a step (mixing step) of mixing the nickel compound and a compound containing molybdenum and sodium to form the mixture prior to the calcination step, and can include a step (calcination step) of calcining the mixture.

[0061]

The compound containing molybdenum and sodium, which is suitable as the flux agent, can be produced, for example, using the molybdenum compound and the sodium compound, which are cheaper and more easily available, as raw materials in the calcination step. Here, both when the molybdenum compound and the sodium compound are used as the flux agent and when the compound containing molybdenum and sodium is used as the flux agent are combined and regarded as when the molybdenum compound and the sodium compound are used as the flux agent, that is, in the presence of the molybdenum compound and the sodium compound.

[0062]

By calcining the nickel compound in the presence of the molybdenum compound and the potassium compound, or in the presence of the molybdenum compound and the sodium compound, the nickel oxide particles having a high molybdenum content can be easily obtained, and the particle diameter of the nickel oxide particles produced can be easily adjusted. The reason is not clear, but the following reasons can be considered. For example, since K_2MoO_4 and Na_2MoO_4 are stable compounds and are difficult to volatilize in the calcination step, they are unlikely to be accompanied by a rapid reaction in a volatilization step, and growth of the nickel oxide particles can be easily controlled. Further, it is considered that the molten K_2MoO_4 and

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Na_2MoO_4 exert a function like a solvent, and for example, by increasing a reaction time, a value of the particle diameter can be increased.

[0063]

In the production method of the embodiment, the molybdenum compound is used as the flux agent. Hereinafter, in this specification, the production method using the molybdenum compound as the flux agent may be simply referred to as the "flux method". Note that after the molybdenum compound reacts with the nickel compound at a high temperature to form nickel molybdate by such calcination, when the nickel molybdate is further decomposed into nickel and molybdenum oxide at a higher temperature, it is considered that the molybdenum compound is incorporated into the nickel oxide particles. It is considered that the molybdenum oxide is sublimated and removed from the system, and in this step, the molybdenum compound and the nickel compound react to form the molybdenum compound in the surface layer of the nickel oxide particles. Regarding formation mechanism of the molybdenum compound contained in the nickel oxide particles, more specifically, it is considered that Mo-O-Ni is formed in the surface layer of the nickel oxide particles by reaction of molybdenum and Ni atoms, Mo is desorbed by high-temperature calcination, and the molybdenum oxide, a compound having a Mo-O-Ni bond, or the like is formed in the surface layer of the nickel oxide particles.

[0064]

The molybdenum oxide that is not incorporated into the nickel oxide particles can also be recovered by sublimation and reused. In this way, an amount of the molybdenum oxide adhering to the surface of the nickel oxide particles can be reduced, and original properties of the nickel oxide particles can be maximized.

[0065]

On the other hand, the alkali metal salt of the molybdenum oxoanion does not vaporize even in a calcination temperature range and can be easily recovered by washing after calcination, so that an amount of the molybdenum compound released to outside a calcining furnace is also reduced, and production cost can also be significantly reduced.

[0066]

In the above flux method, for example, when the molybdenum compound and the potassium compound are used in combination, it is considered that the molybdenum compound and the potassium compound first react to form the potassium molybdate. At the same time, it

is considered that the molybdenum compound reacts with the nickel compound to form the nickel molybdate. Then, for example, the nickel molybdate is decomposed in the presence of potassium molybdate in a liquid phase to grow crystals, so that the nickel oxide particles having a large particle size and a high molybdenum content can be easily obtained while suppressing evaporation of flux (sublimation of MoO_3) described above.

[0067]

(Metal compound)

A metal compound can be used at a time of calcination if desired. The production method of the embodiment can include a step (mixing step) of mixing the nickel compound, the molybdenum compound, the potassium compound, and the metal compound to form the mixture prior to the calcination step, and can include a step (calcination step) of calcining the mixture.

[0068]

The metal compound is not particularly limited, but preferably contains at least one selected from a group including Group II metal compounds and Group III metal compounds.

[0069]

Examples of the Group II metal compounds include magnesium compounds, calcium compounds, strontium compounds, barium compounds and the like.

[0070]

Examples of the Group III metal compounds include scandium compounds, yttrium compounds, lanthanum compounds, cerium compounds and the like.

[0071]

The above-mentioned metal compound means an oxide, a hydroxide, a carbonate, or a chloride of a metal element. For example, in the case of the yttrium compound, yttrium oxide (Y_2O_3), yttrium hydroxide, and yttrium carbonate can be mentioned. Of these, the metal compound is preferably an oxide of the metal element. Note that the metal compound contains an isomer.

[0072]

Of these, the metal compound of period 3 element, the metal compound of period 4 element, the metal compound of period 5 element, and the metal compound of period 6 element are preferable, the metal compound of the 4th period element and the metal compound of period 5 element are more preferable, and the metal compound of period 5 element is further preferable. Specifically, the magnesium compound, the calcium compound, the yttrium compound, and the

lanthanum compound are preferably used, the magnesium compound, the calcium compound, and the yttrium compound are more preferably used, and the yttrium compound is particularly preferably used.

[0073]

The metal compound is preferably used in a proportion of, for example, 0.0 mass% or more and 1.2 mass% or less (for example, 0 mol% or more and 1 mol% or less) with respect to a total amount (total mass or total molar amount) of the nickel compounds used in the mixing step.

[0074]

In the production method of the embodiment, blending amounts of the nickel compound and the molybdenum compound are not particularly limited, but preferably 35 mass% or more of the nickel compound and 65 mass% or less of the molybdenum compound are mixed with respect to 100 mass% of the mixture to form the mixture, and the mixture can be calcined. More preferably, 40 mass% or more and 90 mass% or less of the nickel compound and 0.5 mass% or more and 60 mass% or less of the molybdenum compound are mixed with respect to 100 mass% of the mixture to form the mixture, and the mixture can be calcined. Even more preferably, 42 mass% or more and 50 mass% or less of the nickel compound and 38 mass% or more and 50 mass% or less of the molybdenum compound are mixed with respect to 100 mass% of the mixture to form the mixture, and the mixture can be calcined.

[0075]

In the production method of the embodiment, a value of a molar ratio (molybdenum/nickel) of molybdenum atom in the molybdenum compound and nickel atom in the nickel compound is preferably 0.01 or more, more preferably 0.05 or more, even more preferably 0.10 or more, and particularly preferably 0.30 or more.

An upper limit value of the molar ratio of the molybdenum atom in the molybdenum compound and the nickel atom in the nickel compound may be appropriately determined, but from a viewpoint of reducing the amount of molybdenum compound used and improving production efficiency, for example, the value of the above molar ratio (molybdenum/nickel) may be 5.00 or less, 3.00 or less, 1.00 or less, or 0.50 or less.

As an example of a numerical range of the molar ratio (molybdenum/nickel), for example, the value of molybdenum/nickel may be 0.01 or more and 5.00 or less, 0.05 or more and 3.00 or less, 0.10 or more and 1.00 or less, and 0.30 or more and 0.50 or less.

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[0076]

It should be noted that as the amount of molybdenum used with respect to the nickel is increased, the nickel oxide particles having a large particle size shown in the above particle size distribution tend to be obtained.

[0077]

By using various compounds in the above range, the amount of the molybdenum compound contained in the nickel oxide particles obtained becomes more appropriate, and the nickel oxide particles having a controlled particle size can be easily obtained.

[0078]

[Calcination step]

The calcination step is a step of calcining the mixture. The nickel oxide particles according to the embodiment can be obtained by calcining the mixture. As described above, the production method is called the flux method.

[0079]

The flux method is classified as a solution method. More specifically, the flux method is a method of crystal growth utilizing the fact that a crystal-flux two-component phase diagram shows a eutectic type. A mechanism of the flux method is presumed to be as follows. That is, when a mixture of solute and the flux is heated, the solute and the flux become a liquid phase. At this time, since the flux is a fusing agent, in other words, since a solute-flux two-component phase diagram shows a eutectic type, the solute melts at a temperature lower than its melting point to form the liquid phase. If the flux is evaporated in this state, concentration of the flux is reduced, in other words, an effect on lowering the melting point of the solute by the flux is reduced, and the evaporation of the flux acts as a driving force to cause crystal growth of the solute (flux evaporation method). Note that the solute and the flux can also cause the crystal growth of the solute by cooling the liquid phase (slow cooling method).

[0080]

The flux method has merits such as being able to grow the crystals at a temperature much lower than the melting point, being able to precisely control a crystal structure, and being able to form a polyhedral crystal having an automorphic shape.

[0081]

In production of the nickel oxide particles by the flux method using the molybdenum compound as the flux, the mechanism is not always clear, but for example, it is presumed that the

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mechanism is as follows. That is, when the nickel compound is calcined in the presence of the molybdenum compound, the nickel molybdate is first formed. At this time, as can be understood from the above description, the nickel molybdate grows nickel oxide crystals at a temperature lower than the melting point of the nickel oxide. Then, for example, by evaporating the flux, the nickel molybdate is decomposed to grow the crystals, so that the nickel oxide particles can be obtained. That is, the molybdenum compound functions as the flux, and the nickel oxide particles are produced via an intermediate called the nickel molybdate.

[0082]

By the above flux method, the nickel oxide particles containing molybdenum and in which the molybdenum is unevenly distributed in the surface layer of the nickel oxide particles can be produced.

[0083]

A method of calcination is not particularly limited, and the calcination can be performed by a known and commonly used method. When the calcination temperature exceeds 800°C, it is considered that the nickel compound and the molybdenum compound react to form the nickel molybdate. Further, it is considered that when the calcination temperature becomes 950°C or higher, the nickel molybdate is decomposed to form the nickel oxide particles. Further, in the nickel oxide particles, it is considered that the molybdenum compound is incorporated into the nickel oxide particles when the nickel molybdate is decomposed into the nickel oxide and the molybdenum oxide.

[0084]

Further, a state of the nickel compound and the molybdenum compound at the time of calcination is not particularly limited, and the molybdenum compound may be present in the same space where the molybdenum compound can act on the nickel compound. Specifically, the state may be a simple mixture in which powders of the molybdenum compound and powders of the nickel compound are mixed, a mechanical mixture using a crusher or the like, a mixture using a mortar or the like, and may be a mixture in a dry state or in a wet state.

[0085]

Conditions of the calcination temperature are not particularly limited, and are appropriately determined in consideration of a target particle size of the nickel oxide particles, formation of the molybdenum compound in the nickel oxide particles, the shape of the nickel

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oxide particles, and the like. The calcination temperature may be 900°C or higher, which is close to a decomposition temperature of the nickel molybdate, 950°C or higher, or 1000°C or higher.

[0086]

As the calcination temperature is higher, the nickel oxide particles having a controlled particle shape and a large particle size tend to be easily obtained. From a viewpoint of efficiently producing such nickel oxide particles, the calcination temperature is preferably 950°C or higher, more preferably 1000°C or higher, even more preferably 1100°C or higher, and particularly preferably 1200°C or higher.

[0087]

Generally, when trying to control the shape of the nickel oxide particles obtained after calcination, it is necessary to perform the high-temperature calcination at a temperature of over 1900°C, which is close to the melting point of the nickel oxide, but there is a big problem in industrial applications from viewpoints of load on the calcining furnace and fuel cost.

[0088]

According to the embodiment of the present invention, for example, even if the maximum calcination temperature for calcining the nickel compound is 1600°C or lower, the nickel oxide particles can be efficiently formed at low cost.

[0089]

Further, according to the production method of the embodiment, even if the calcination temperature is 1600°C or lower, which is much lower than the melting point of the nickel oxide, the nickel oxide particles having an automorphic shape can be formed regardless of a shape of a precursor. From this point of view, the calcination temperature is preferably 1500°C or lower, more preferably 1400°C or lower, and even more preferably 1300°C or lower.

[0090]

As an example, a numerical range of the calcination temperature at which the nickel compound is calcined in the calcination step may be 900°C or higher and 1600°C or lower, 900°C or higher and 1500°C or lower, 950°C or higher and 1400°C or lower, 1000°C or higher and 1300°C or lower, or 1100°C or higher and 1300°C or lower.

[0091]

From a viewpoint of the production efficiency, a heating rate may be 20°C/hour or more and 600°C/hour or less, 40°C/hour or more and 500°C/hour or less, and 80°C/hour or more and

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400°C/hour or less.

[0092]

Regarding a calcination time, the calcination is preferably performed such that a raising time to a predetermined calcination temperature is in a range of 15 minutes or more and 10 hours or less, and a holding time at the calcination temperature is in a range of 5 minutes or more and 30 hours or less. In order to efficiently form the nickel oxide particles, it is more preferred that the holding time at the calcination temperature is 2 hours or more and 24 hours or less.

[0093]

As an example, by selecting the conditions of the calcination temperature of 900°C or higher and 1600°C or lower and the holding time at the calcination temperature of 2 hours or more and 24 hours or less, the nickel oxide particles of the embodiment containing molybdenum can be easily obtained.

[0094]

Calcination atmosphere is not particularly limited as long as an effect of the production method of the embodiment can be obtained, but for example, oxygen-containing atmosphere such as air or oxygen or an inert atmosphere such as nitrogen, argon or carbon dioxide is preferable, and air atmosphere is more preferable when considering the cost.

[0095]

An apparatus for calcination is also not necessarily limited, and a so-called calcining furnace can be used. The calcining furnace is preferably made of a material that does not react with sublimated molybdenum oxide, and it is preferable to use a highly airtight calcining furnace so that the molybdenum oxide can be used efficiently.

[0096]

[Molybdenum removal step]

The production method of the embodiment may further include a molybdenum removal step of removing at least a part of molybdenum after the calcination step, if necessary.

[0097]

As described above, since the molybdenum is sublimated during calcination, it is possible to control the molybdenum content present in the surface layer of the nickel oxide particles, and to control the molybdenum content and its existence state in other than the surface layer (inner layer) of the nickel oxide particles, by controlling the calcination time, the calcination temperature, and the like.

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[0098]

The molybdenum can adhere to the surface of the nickel oxide particles. As a means other than the above sublimation, the molybdenum can be removed by washing with water, an aqueous ammonia solution, an aqueous sodium hydroxide solution or the like.

[0099]

At this time, the molybdenum content in the nickel oxide particles can be controlled by appropriately changing concentration and used amount of the water, the aqueous ammonia solution, or the aqueous sodium hydroxide solution used, and a washing site, a washing time or the like.

[0100]

[Pulverizing step]

In a calcined product obtained through the calcination step, the nickel oxide particles may aggregate, and the calcined product may not meet a range of particle diameter suitable for applications to be considered. Therefore, the nickel oxide particles may be pulverized to satisfy the range of suitable particle diameter, if necessary.

[0101]

A method for pulverizing the calcined product is not particularly limited, and conventionally known pulverizing methods such as ball mill, jaw crusher, jet mill, disc mill, Spectromill, grinder, and mixer mill can be used.

[0102]

[Classification step]

The calcined product containing the nickel oxide particles obtained in the calcination step may be appropriately classified in order to adjust a range of the particle size. A "classification process" refers to an operation of grouping particles based on the size of the particles.

[0103]

The classification may be either wet or dry, but from a viewpoint of productivity, the dry classification is preferable. The dry classification includes classification by sieving, wind classification by a difference between centrifugal force and fluid drag, and the like, but from a viewpoint of classification accuracy, the wind classification is preferable, and can be performed by using a classifier using Coanda effect, such as an airflow classifier, a swirling airflow classifier, a forced vortex centrifugal classifier, and a semi-free vortex centrifugal classifier.

[0104]

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The above-mentioned pulverization step and classification step can be performed at a necessary stage. For example, the average particle diameter of the nickel oxide particles to be obtained can be adjusted by the presence or absence of pulverizing and classification, and selection of their conditions.

[0105]

In the nickel oxide particles of the embodiment or the nickel oxide particles obtained by the production method of the embodiment, the nickel oxide particles having little or no aggregation are likely to exhibit their original properties and are superior in their own handleability, and when they are used by being dispersed in a medium to be dispersed, they are preferable from the viewpoint of being more excellent in dispersibility.

[0106]

Note that according to the production method of the above-described embodiment, since the nickel oxide particles having little or no aggregation can be easily produced, it has an excellent advantage that the nickel oxide particles having excellent desired properties can be produced with high productivity without performing the above-mentioned pulverization step or classification step.

[0107]

Since the nickel oxide particles of the embodiment or the nickel oxide particles obtained by the production method of the embodiment have the above-mentioned characteristics, they are preferably used, for example, for an electrode of a solid oxide fuel cell (SOFC) or an electrode of a steam charge device, or the like.

[Examples]

[0108]

Next, the present invention will be described in more detail with reference to Examples, but the present invention is not limited to the following Examples.

[0109]

<Production of nickel oxide particles>

[Comparative Example 1]

3.0 g of nickel oxide (produced by Aladdin) was placed in a crucible and calcined in a ceramic electric furnace at 1100°C for 24 hours. After the temperature was lowered, the crucible was taken out to obtain 3.0 g of green powders.

[0110]

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[Comparative Example 2]

3.0 g of nickel oxide (produced by Aladdin) was placed in the crucible and calcined in the ceramic electric furnace at 1300°C for 24 hours. After the temperature was lowered, the crucible was taken out to obtain 3.0 g of green powders.

[0111]

[Comparative Example 3]

Nickel oxide (produced by Aladdin) was used as it was as a sample of Comparative Example 3.

[0112]

[Example 1]

3.0 g of nickel oxide (produced by Aladdin), 2.71 g of molybdenum trioxide (produced by Chengdu Hongbo Industrial Co., Ltd.), 1.3 g of potassium carbonate, and 0.015 g of yttrium oxide were mixed in a mortar to obtain a mixture. The obtained mixture was placed in the crucible and calcined in the ceramic electric furnace at 1300°C for 24 hours. After the temperature was lowered, the crucible was taken out to obtain 4.1 g of green powders. Subsequently, 4.1 g of the obtained green powders were suspended in 30 g of ion-exchanged water, stirred for two hours, filtered and washed to obtain 2.8 g of green powders.

[0113]

[Example 2]

3.0 g of nickel oxide (produced by Aladdin) and 3.0 g of sodium molybdate dihydrate (produced by Chengdu Hongbo Industrial Co., Ltd.) were mixed in the mortar to obtain the mixture. The obtained mixture was placed in the crucible and calcined in the ceramic electric furnace at 1300°C for 24 hours. After the temperature was lowered, the crucible was taken out to obtain 4.4 g of green powders. Subsequently, 4.4 g of the obtained green powders were suspended in 30 g of ion-exchanged water, stirred for two hours, filtered and washed to obtain 2.9 g of green powder.

[0114]

<Evaluation>

The powders obtained in Examples 1 and 2 and Comparative Examples 1 to 3 were used as sample powders and evaluated as follows.

[0115]

[Measurement of crystallite diameter]

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Using an X-ray diffractometer (SmartLab manufactured by Rigaku Corporation) equipped with a high-intensity high-resolution crystal analyzer (CALSA) as a detector, the measurement was performed by powder X-ray diffraction (2θ/θ method) under the following measurement conditions. Analysis was performed using CALSA function of analysis software (PDXL) manufactured by Rigaku Corporation, the crystallite diameter of the [111] plane was calculated using the Scherrer equation from the half width of the peak appearing near 2θ = 37.3°, and the crystallite diameter of the [200] plane was calculated using the Scherrer equation from the half width of the peak appearing near 2θ = 43.3°. Results are shown in Table 1.

[0116]

(Measurement conditions of powder X-ray diffraction method)

Tube voltage: 45 kV

Tube current: 200 mA

Scan speed: 0.05°/min

Scan range: from 10° to 70°

Step: 0.002°

βs: 20 rpm

Apparatus standard width: 0.026° calculated using standard silicon powder (NIST, 640d) produced by the National Institute of Standards and Technology was used.

[0117]

[Crystal structure analysis: X-ray diffraction (XRD) method]

The sample powders were filled in a holder for a measurement sample having a depth of 0.5 mm, set in a wide-angle X-ray diffraction (XRD) apparatus (Ultima IV manufactured by Rigaku Corporation), and the measurement was performed under conditions of Cu/Kα ray, 40 kV/40 mA, scanning speed 2°/min, and scanning range of 10° to 70°.

[0118]

[Measurement of particle size distribution]

Using a laser diffraction type dry particle size distribution meter (HELOS (H3355) & RODOS manufactured by Japan Laser Corporation), the particle size distribution of the sample powders was measured by the dry method under conditions of a dispersion pressure of 3 bar and a pulling pressure of 90 mbar. The particle diameter at a point where a distribution curve of cumulative volume% intersects a horizontal axis of 10% from the small particle side was defined

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as D_{10}, the particle diameter at a point where the distribution curve intersects the horizontal axis of 50% was defined as D_{50}, and the particle diameter at a point where the distribution curve intersects the horizontal axis of 90% from the small particle side was defined as D_{90}, and they were determined.

[0119]

[X-ray fluorescence (XRF) analysis]

Using a fluorescent X-ray analyzer Primus IV (manufactured by Rigaku Corporation), about 70 mg of the sample powders were placed on a filter paper, were covered with a PP film, and the X-ray fluorescence (XRF) analysis was performed under the following conditions.

[0120]

(Measurement conditions)

EZ scan mode

Elements to be measured: F to U

Measurement time: standard

Measurement diameter: 10 mm

Residual (Balance component): None

[0121]

The results of the NiO content (N_1) with respect to 100 mass% of the nickel oxide particles and the MoO_3 content (M_1) with respect to 100 mass% of the nickel oxide particles were obtained by XRF analysis.

[0122]

[XPS surface analysis]

For surface element analysis of the sample powders, X-ray Photoelectron spectroscopy (XPS) measurement was performed using QUANTERA SXM manufactured by ULVAC-PHI, Inc. and monochromatic Al-Kα as an X-ray source. In an area measurement of 1000 μm square, an average value of n = 3 measurement was obtained in atom% for each element.

[0123]

By converting the nickel content in the surface layer and the molybdenum content in the surface layer of the nickel oxide particles obtained by XPS analysis into oxides, the NiO content (N_2) (mass%) with respect to 100 mass% of the surface layer of the nickel oxide particles and the MoO_3 content (M_2) (mass%) with respect to 100 mass% of the surface layer of the nickel oxide particles were determined.

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[0124]

<Results>

Table 1 shows each value obtained by the above evaluation. Note that "N.D." is an abbreviation for not detected, and indicates that it is not detected.

[0125]

[Table 1]

				Comparative Example 1	Comparative Example 2	Comparative Example 3	Example 1	Example 2
Production Conditions		NiO	g	3.00	3.00	-	3.00	3.00
		MoO_3	g	-	-		2.71	-
		$Na_2MoO_4 \cdot 2H_2O$	g	-	-		-	3.00
		K_2CO_3	g	-	-		1.30	-
		Y_2O_3	g	-	-		0.015	-
		Mo/Ni	molar ratio	-	-		0.47	0.31
		Calcination temperature	°C	1100	1300		1300	1300
		Calcination time	hour	24	24		24	24
Evaluation	Particle size distribution	D_{10}	μm	1.02	2.90	0.37	39.99	6.10
		D_{50}	μm	3.07	5.71	1.26	61.98	13.87
		D_{90}	μm	12.85	11.11	4.32	93.14	38.76
	Crystallite diameter	[111] plane 37.3°	nm	230	289	88	746	269
		[200] plane 43.3°	nm	215	301	96	292	383
	XRF	NiO (N_1)	mass%	99.90	99.70	99.80	95.70	99.60
		MoO_3 (M_1)	mass%	0.07	0.03	N.D.	1.49	0.05
	XPS	NiO (N_2)	mass%	97.90	71.50	98.10	53.52	53.13
		MoO_3 (M_2)	mass%	N.D.	N.D.	N.D.		
	MoO_3 surface layer uneven distribution ratio (M_2/M_1)			-	-	-	22.77	583.62

[0126]

SEM images of the powders of the above Examples and Comparative Examples obtained by photographing with a scanning electron microscope (SEM) are shown in Figs. 1 to 4. Granular particles were observed in each of Examples and Comparative Examples.

[0127]

Results of XRD analysis are shown in Fig. 5. Each peak derived from the nickel oxide (NiO) was observed in each sample of Examples and Comparative Examples.

[0128]

From the results of the above SEM observation and XRD analysis, it was confirmed that the powders obtained in Examples and Comparative Examples were the nickel oxide particles

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containing nickel oxide.

[0129]

Further, as shown in an image on the right side of Fig. 2, it was confirmed that in the nickel oxide particles of Example 2, a structure in which plates were laminated on the surface of the granular particles is formed. Details of a mechanism of this structure are unknown, but it can be expected that a surface area is increased and the catalytic activity is increased.

[0130]

According to comparison of Examples 1 and 2, as the ratio of the molar amount of molybdenum to the molar amount of nickel (Mo/Ni) increases, the particles having a large particle size (each value of D_{10}, D_{50}, and D_{90}) and large crystallite diameter ([111] plane and [200] plane) tend to be obtained. Therefore, it was shown that the particle size of the nickel oxide particles to be produced can be easily controlled by calcining the nickel compound in the presence of the molybdenum compound.

[0131]

Further, as shown in Table 1, from the results of the MoO_3 content (M_1) and the MoO_3 content (M_2), the nickel oxide particles of Examples 1 and 2 contain molybdenum on the surface, and it is expected that various actions of molybdenum, such as catalytic activity will be exerted.

[0132]

Further, as shown in Table 1, from the results of the surface layer uneven distribution ratio (M_2/M_1) of the MoO_3 content (M_2) to the MoO_3 content (M_1), in the nickel oxide particles of Examples 1 and 2, the molybdenum oxide content in the surface layer of the nickel oxide particles determined by XPS surface analysis is greater than the molybdenum oxide content determined by XRF analysis. Therefore, it was confirmed that molybdenum was unevenly distributed in the surface layer of the nickel oxide particles, and it can be expected that various actions of molybdenum will be effectively exerted.

[0133]

Each configuration in each embodiment, a combination thereof, and the like are examples, and the configuration can be added, omitted, replaced, and other changes can be made without departing from the spirit of the present invention. Further, the present invention is not limited by each embodiment, but is limited only by the scope of the claims.

Industrial Applicability

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[0134]

According to the nickel oxide particles and the method for producing the nickel oxide particles of the embodiment, the nickel oxide particles having a controlled particle diameter and particle size distribution can be obtained.

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CLAIMS

1. Nickel oxide particles comprising molybdenum.

2. The nickel oxide particles according to claim 1, wherein the molybdenum is unevenly distributed in a surface layer of the nickel oxide particles.

3. The nickel oxide particles according to claim 1 or 2, wherein a crystallite diameter of a [100] plane of the nickel oxide particles is 240 nm or more.

4. The nickel oxide particles according to any one of claims 1 to 3, wherein a crystallite diameter of a [101] plane of the nickel oxide particles is 220 nm or more.

5. The nickel oxide particles according to any one of claims 1 to 4, wherein a median diameter D_{50} of the nickel oxide particles calculated by a laser diffraction/scattering method is 10.00 μm or more and 1000.00 μm or less.

6. The nickel oxide particles according to any one of claims 1 to 5, wherein

NiO content N_1 with respect to 100 mass% of the nickel oxide particles determined by XRF analysis of the nickel oxide particles is 60.00 mass% or more and 99.60 mass% or less, and

MoO_3 content M_1 with respect to 100 mass% of the nickel oxide particles determined by XRF analysis of the nickel oxide particles is 0.04 mass% or more and 40.00 mass% or less.

7. The nickel oxide particles according to any one of claims 1 to 6, wherein

NiO content N_2 with respect to 100 mass% of a surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles is 10.00 mass% or more and 70.00 mass% or less, and

MoO_3 content M_2 with respect to 100 mass% of the surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles is 20.00 mass% or more and 40.00 mass% or less.

8. The nickel oxide particles according to any one of claims 1 to 7, wherein a surface layer uneven distribution ratio M_2/M_1 of MoO_3 content M_2 with respect to 100 mass% of a surface layer of the nickel oxide particles determined by XPS surface analysis of the nickel oxide particles to MoO_3 content M_1 with respect to 100 mass% of the nickel oxide particles determined

by XRF analysis of the nickel oxide particles is 0.05 or more and 1000.00 or less.

9. A method for producing the nickel oxide particles according to any one of claims 1 to 8, comprising calcining a nickel compound in presence of a molybdenum compound.

10. The method for producing the nickel oxide particles according to claim 9, wherein the molybdenum compound is at least one compound selected from a group including molybdenum trioxide, lithium molybdate, potassium molybdate and sodium molybdate.

11. The method for producing the nickel oxide particles according to claim 9 or 10, wherein a calcination temperature is 800°C or higher and 1600°C or lower.

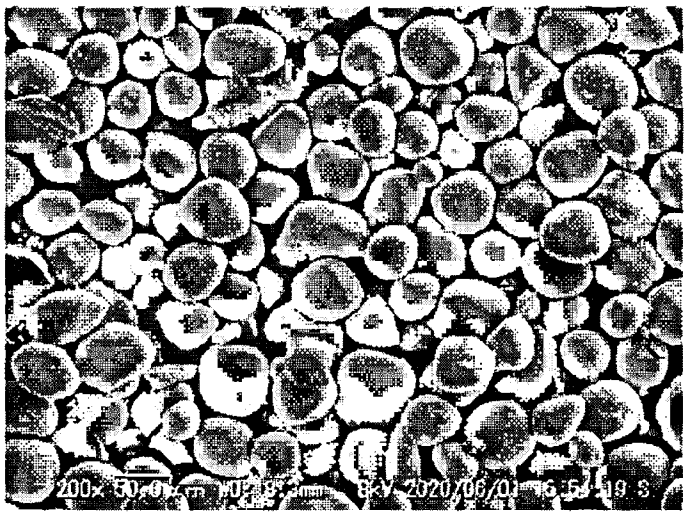

FIG. 1

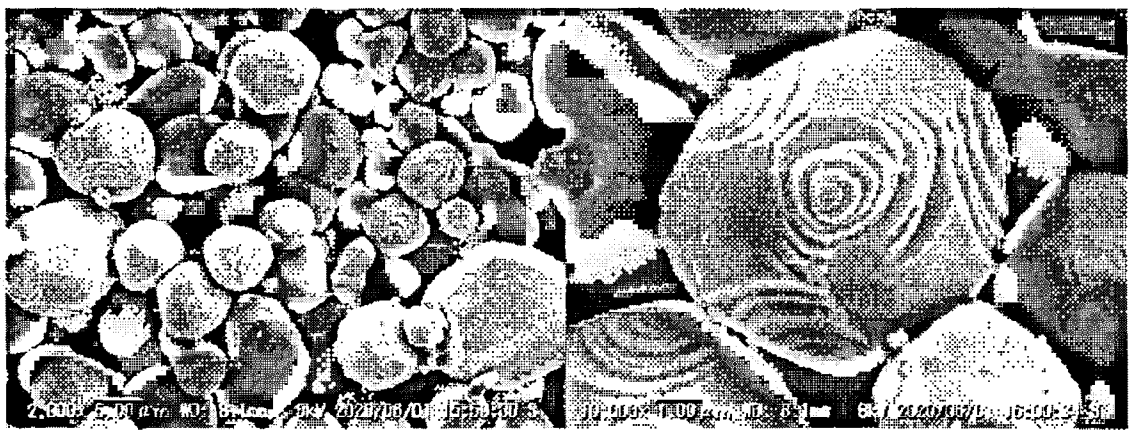

FIG. 2

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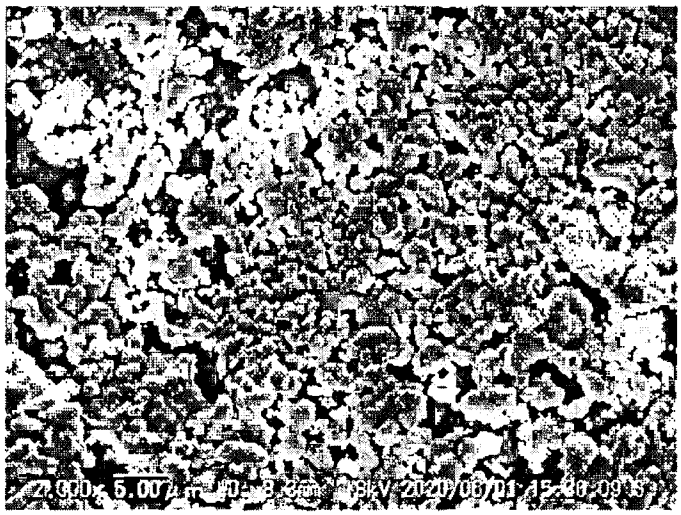

FIG. 3

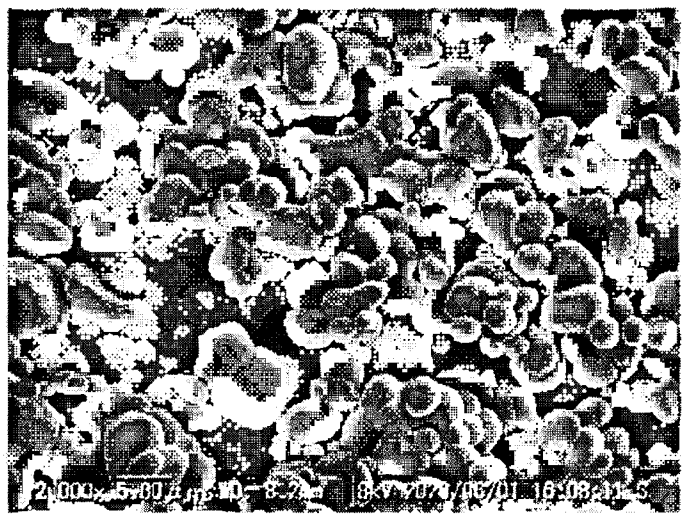

FIG. 4

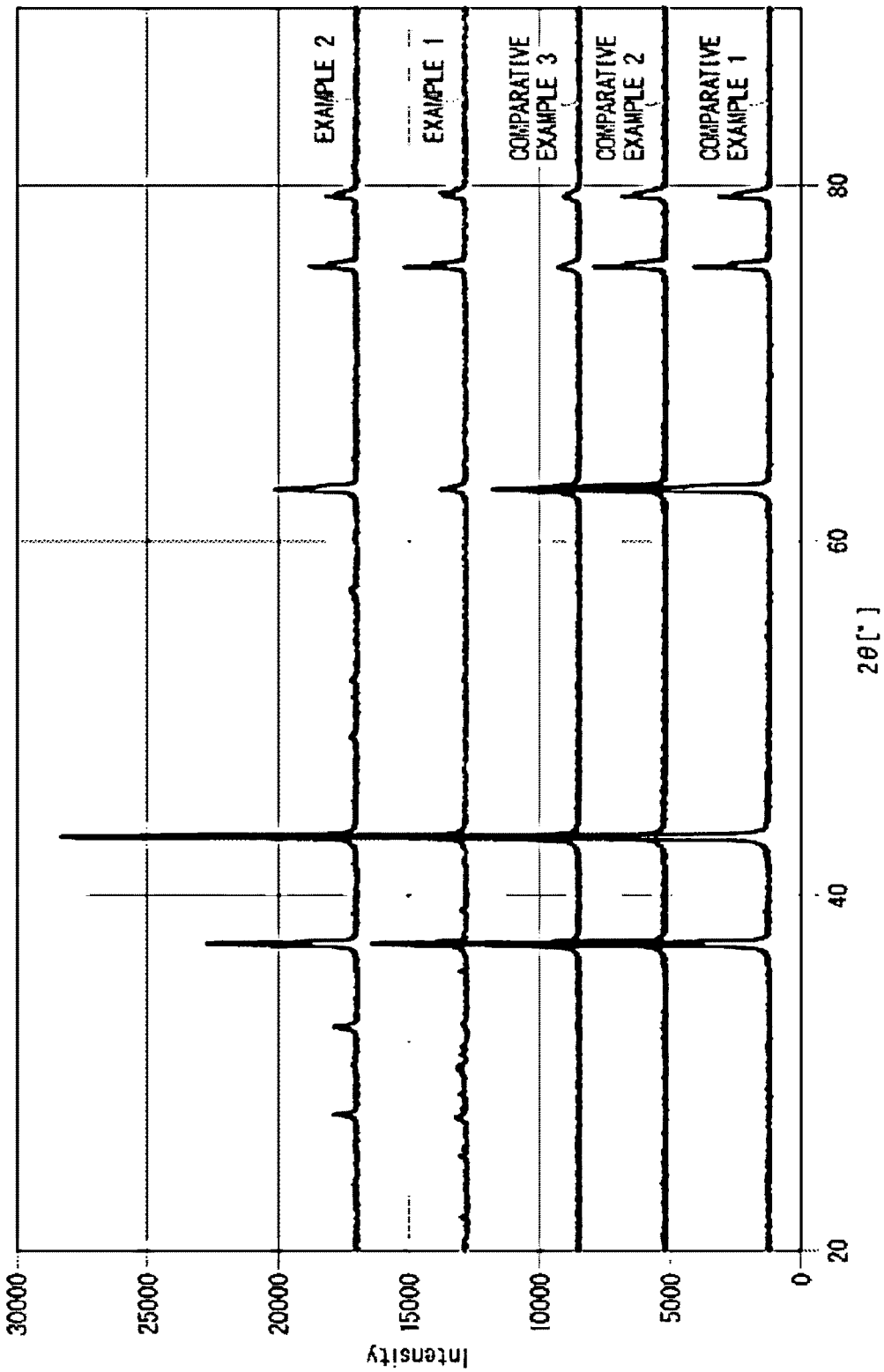
EXAMPLE 2
EXAMPLE 1
COMPARATIVE EXAMPLE 3
COMPARATIVE EXAMPLE 2
COMPARATIVE EXAMPLE 1
Intensity
30000
25000
20000
15000
10000
5000
0
20
40
60
80
2θ[°]

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2021/096527

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/90(2006.01)i; B01J 27/19(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)

H01M, B01J

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

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

WPI, EPODOC, CNPAT, CNKI: NiO, nickel, oxide, Mo, molybdenum, Ni2O3, NiO2, MoO3, molybdate, oxo+, calcin+, bak +, sinter+, catalyst+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 106159288 A (CHINESE ACAD. SCI. PHYSICS INST.) 23 November 2016 (2016-11-23) description, paragraphs 0018-0104	1-11
A	US 3972954 A (PHILLIPS PETROLEUM COMPANY) 03 August 1976 (1976-08-03) the whole document	1-11
A	US 2013105364 A1 (SHELL OIL COMPANY) 02 May 2013 (2013-05-02) the whole document	1-11
A	US 2013284640 A1 (SHELL OIL COMPANY) 31 October 2013 (2013-10-31) the whole document	1-11

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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	Date of mailing of the international search report
17 January 2022	**27 January 2022**
Name and mailing address of the ISA/CN **National Intellectual Property Administration, PRC** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China** Facsimile No. **(86-10)62019451**	Authorized officer **JIANG,Feng** Telephone No. **86-(10)-53961285**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2021/096527

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	106159288	A	23 November 2016	None			
US	3972954	A	03 August 1976	US	4094819A	A	13 June 1978
US	2013105364	A1	02 May 2013	IN	3464CHN2014	A	09 October 2015
				CN	109107594	A	01 January 2019
				KR	20140095508	A	01 August 2014
				KR	102025447	B1	25 September 2019
				ZA	201402957	B	25 February 2015
				JP	2015501215	A	15 January 2015
				JP	6092234	B2	08 March 2017
				EP	2771113	A1	03 September 2014
				EP	2771113	B1	23 January 2019
				CA	2853104	A1	02 May 2013
				CA	2853104	C	02 June 2020
				WO	2013063219	A1	02 May 2013
				CN	103974770	A	06 August 2014
				DK	2771113	T3	15 April 2019
				RU	2014121253	A	10 December 2015
				RU	2637508	C2	05 December 2017
				BR	112014010043	A2	13 June 2017
				BR	112014010043	A8	20 June 2017
US	2013284640	A1	31 October 2013	CA	2871356	A1	31 October 2013
				CA	2871356	C	30 June 2020
				RU	2014147561	A	20 June 2016
				RU	2636150	C2	21 November 2017
				KR	20150008885	A	23 January 2015
				KR	102139390	B1	30 July 2020
				JP	2015519193	A	09 July 2015
				JP	6396289	B2	26 September 2018
				EP	2841198	A2	04 March 2015
				BR	112014026756	A2	27 June 2017
				SG	10201608662P	A	29 December 2016
				WO	2013163126	A2	31 October 2013
				WO	2013163126	A3	21 November 2013
				SG	11201406650W	A	27 November 2014
				CN	104394982	A	04 March 2015
				US	9879187	B2	30 January 2018
				ZA	201407488	B	25 November 2015