

A SELECTIVE NICKEL BASED HYDROGENATION CATALYST AND THE PREPARATION THEREOF

FIELD OF THE INVENTION

The present invention relates to a selective nickel-based hydrogenation catalyst and the preparation thereof. The catalyst is useful in selective hydrogenation of medium or low distillate oil, in particular, in the first-stage selective hydrogenation process of pyrolysis gasoline distillate.

BACKGROUND OF THE INVENTION

Pyrolysis gasoline is the by-product of steam cracking to make ethylene, which approximately comprises more than 50% of the production capacity of ethylene. Pyrolysis gasoline contains highly unsaturated hydrocarbons, such as diolefin, styrene and the like, which can be converted into corresponding monoolefin by selective hydrogenation. With the increasing ethylene production capability in China, the hydrogenation of pyrolysis gasoline has developed toward the hydrogenation of full distillate using nickel-based catalyst. Due to the variability of the pyrolysis gasoline raw materials and the differences in pyrolysis apparatus and pyrolysis modes, the pyrolysis gasoline raw materials are deteriorated, and the hydrogenation load and the content of impurity such as arsenic are increased, thereby causing the inferior performance of palladium-based catalyst for first-stage hydrogenation. For noble metal catalyst, its arsenic and colloid resistance as well as water resistance is low, since the impurity arsenic tends to occupy the empty orbital of Pd, and Pd is located on the surface layer of the catalyst with a content of only parts per thousand. For non-noble metal catalyst, it has certain arsenic tolerance and colloid and water resistance due to the structural difference and high metal content; moreover, it has relatively remarkable price advantage. Thus, there is need of the market and technical competition to develop a new nickel-based catalyst for first-stage hydrogenation of full distillate pyrolysis gasoline.

US3472763 reports a Ni/Al₂O₃ catalyst for the selective hydrogenation of diolefin, comprising 1-20% nickel as active component, 1-5% MoO₃ as aids, 1-5% alkali metal and alkaline earth metal as aids, and having a pore volume of more than 0.4ml/g and a specific surface area of more than 30m²/g. This catalyst is prepared by impregnating the Al₂O₃ carrier with the aqueous solution of above-mentioned active component and aids. CN1218822A reports a Ni/Al₂O₃ catalyst suitable for the selective hydrogenation of pyrolysis gasoline distillates. This catalyst is prepared by loading nickel on alumina carrier comprising lithium or alkaline earth metal. However, this catalyst is not good at withstanding the hydrogenation load and its hydrogenation stability is to be improved.

An excellent selective hydrogenation catalyst should have higher hydrogenation activity and better selectivity. More importantly, it should have good stability. That is to say, it is necessary for such catalyst to have capability to resist impurity and

colloid, thereby prolonging its lifetime.

SUMMARY OF THE INVENTION

5 The aim of the present invention is to develop a nickel-based Al_2O_3 supported catalyst for selective hydrogenation of diolefin. The catalyst has good hydrogenation performance, especially has good hydrogenation stability, and can be applied to the selective hydrogenation of full distillate pyrolysis gasoline.

10 The selective nickel-based hydrogenation catalyst of the present invention, with alumina as carrier, is characterized in that based on the total weight of the catalyst, it comprises:

- 14-20% nickel oxide as active component;
- 1-8% lanthanum oxide and/or cerium oxide;
- 1-8% VIB group element oxide as aids;
- 15 2-8% silica;
- 1-8% alkaline earth metal oxide;

wherein said catalyst has a specific surface area of $60\text{-}150\text{ m}^2/\text{g}$ and a pore volume of $0.4\text{-}0.6\text{ ml/g}$. This catalyst is especially useful in the diolefin selective hydrogenation of medium or low distillate oil, in particular, in the diolefin selective hydrogenation of full distillate pyrolysis gasoline.

20 The present invention also provides a method for preparing such catalyst, comprising:

adding silica or its precursor and alkaline earth metal oxide or its precursor into alumina carrier;

25 calcinating at the temperature of $800\text{-}1100^\circ\text{C}$ for 3-6 hours to form the modified alumina carrier;

adding the soluble salts of nickel, lanthanum and/or cerium and VIB group element into water;

30 after fully dissolution, adjusting the pH of the solution to 4-5 to form an impregnating solution;

impregnating the modified alumina carrier with the impregnating solution;

drying at the temperature of $40\text{-}120^\circ\text{C}$; and

calcinating at the temperature of $350\text{-}450^\circ\text{C}$ for 3-6 hours, thereby obtaining the resultant catalyst.

35 In particular, the present invention preferably recommends that the modified alumina carrier is prepared by:

adding silica sol, nitric acid and water into alumina hydrate (pseudo-boehmite);

after kneading and extruding, drying at the temperature of $40\text{-}120^\circ\text{C}$;

calcinating at the temperature of $300\text{-}600^\circ\text{C}$ for 4-6 hours;

40 impregnating the formed carrier with the impregnating solution formed by adding alkaline earth metal oxide into water;

drying at the temperature of $40\text{-}120^\circ\text{C}$; and

calcinating at the temperature of $800\text{-}1100^\circ\text{C}$ for 4-6 hours, thereby forming the modified alumina carrier with desired physical properties.

The catalyst according to the present invention comprises 2-8% silica, which may increase the stability of the catalyst, especially the carrier during calcination. Preferably, the content of silica is 3-4%. Preferably, the content of nickel oxide is 15-19%.

5 The catalyst according to the present invention comprises alkaline earth metal, which may adjust the acidity of the catalyst after calcination and improve the colloid resistance during hydrogenation reaction. Preferably, the alkaline earth metal is magnesium and/or strontium. The content of alkaline earth metal oxide is preferably 2-5%.

10 The lanthanum and/or cerium are added in the form of nitrate dissolved in the impregnating solution so as to improve the hydrogenation activity and stability of the catalyst. Preferably, the content of lanthanum oxide and/or cerium oxide is 3-5%.

The VIB group element is added to improve the hydrogenation activity and impurity (for example, sulfur) resistance of the catalyst. Preferably, the VIB group
15 element is one or more of Cr, Mo and W. The content of VIB group element oxide is preferably 3-6%.

The solution of the active component and aids are impregnated onto the resultant catalyst carrier in twice to increase the dispersity of the active component of the catalyst and improve the activity and stability of catalyst.

20 The compounds of nickel (as active component), magnesium, strontium lanthanum and cerium (as aids) in above-mentioned preparation process may be in the form of sulfate, nitrate and halide and so on. Preferably, they are in the form of nitrate, since nitrate is easily soluble in water to be fully dissolved and form stable solution.

The alumina hydrate, as the starting material for preparing the catalyst according
25 to the present invention, may be alumina hydrates prepared by carbon dioxide method, ammonia method, and nitric acid method and so on. The alumina hydrate prepared by nitric acid method is preferable due to its better hydrogenation performance.

The catalyst according to the present invention should be reduced under hydrogen at the temperature of 350-400°C for 5-10 hours prior to use. During the
30 reduction, the volume ratio of hydrogen to catalyst is 150:1 to 500:1.

DETAILED DESCRIPTION OF THE INVENTION

Source of starting materials:

35 Nickel nitrate: available from Xi'an Chemical Reagent Factory;

Magnesium nitrate and strontium nitrate: available from Shanghai Colloid Chemical Plant;

Cerium nitrate and lanthanum nitrate: available from Shensheng Reagent Factory, Fufeng, Yixing, Jiangsu;

40 Alumina powder: available from Lanhua Xiangxin Additives Factory.

Example 1

140ml water, 5ml nitric acid (the content of which is 60%) and 16ml silica sol (comprising 40% silica) are added to 300g pseudo-boehmite alumina powder. After

kneading and extruding, the formed alumina carrier is dried in air at 120°C, and then calcinated at 560°C for 4 hours. 100g calcinated carrier is impregnated with a solution form by dissolving 26g magnesium nitrate into water, dried in air at 120°C, and calcinated at 1050°C for 4 hours, thereby obtaining the modified Al₂O₃ carrier.

- 5 10g nickel nitrate is added to 20ml water with stirring. While stirring, 2.1g cerium nitrate and 0.3g ammonium molybdate are added. The pH of the solution is adjusted to 4. Then 10g carrier is impregnated with the solution, aged for 12 hours, dried at 120°C, and calcinated at 400°C for 4 hours, thereby obtaining the catalyst.

10 Comparative Example 1

- 140ml water and 5ml nitric acid (the content of which is 60%) are added to 300g pseudo-boehmite alumina powder. After kneading and extruding, the formed alumina carrier is dried in air at 120°C, and then calcinated at 560°C for 4 hours. 100g calcinated carrier is impregnated with a solution formed by dissolving 16.7g
15 magnesium nitrate and 3g strontium nitrate into water, dried in air at 120°C, and calcinated at 1050°C for 4 hours, thereby obtaining the Al₂O₃ carrier.

- 10g nickel nitrate is added to 20ml water with stirring. While stirring, 2.1g cerium nitrate and 0.3g ammonium molybdate are added. The pH of the solution is adjusted to 4. Then 10g carrier is impregnated with the solution, aged for 12 hours,
20 dried at 120°C, and calcinated at 400°C for 4 hours, thereby obtaining the catalyst.

Example 2

- 140ml water, 5ml nitric acid (the content of which is 60%) and 14ml silica sol (comprising 40% silica) are added to 300g pseudo-boehmite alumina powder. After
25 kneading and extruding, the formed alumina carrier is dried in air at 120°C, and then calcinated at 460°C for 4 hours. 100g calcinated carrier is impregnated with a solution formed by dissolving 20g magnesium nitrate and 3.5g strontium nitrate into water, dried in air at 120°C, and calcinated at 1000°C for 4 hours, thereby obtaining the Al₂O₃ carrier.

- 30 8.6g nickel nitrate is added to 20ml water with stirring. While stirring, 1.5g lanthanum nitrate and 0.6g ammonium tungstate are added. The pH of the solution is adjusted to 4. Then 10g carrier is impregnated with the solution, aged for 12 hours, dried at 120°C, and calcinated at 350°C for 4 hours, thereby obtaining the catalyst.

35 Comparative Example 2

- 140ml water, 5ml nitric acid (the content of which is 60%) and 14ml silica sol (comprising 40% silica) are added to 300g pseudo-boehmite alumina powder. After kneading and extruding, the formed alumina carrier is dried in air at 120°C, and calcinated at 1000°C for 4 hours, thereby obtaining the Al₂O₃ carrier.

- 40 8.6g nickel nitrate is added to 20ml water with stirring. While stirring, 1.5g lanthanum nitrate and 0.6g ammonium tungstate are added. The pH of the solution is adjusted to 4. Then 10g carrier is impregnated with the solution, aged for 12 hours, dried at 120°C, and calcinated at 350°C for 4 hours, thereby obtaining the catalyst.

Example 3

140ml water, 5ml nitric acid (the content of which is 60%) and 9ml silica sol (comprising 40% silica) are added to 300g pseudo-boehmite alumina powder. After kneading and extruding, the formed alumina carrier is dried in air at 120°C, and then calcinated at 460°C for 4 hours. 100g calcinated carrier is impregnated with a solution formed by dissolving 15.5g magnesium nitrate into water, dried in air at 120°C, and calcinated at 1030°C for 4 hours, thereby obtaining the Al_2O_3 carrier.

7.9g nickel nitrate is added to 20ml water with stirring. While stirring, 0.63g cerium nitrate, 0.62g lanthanum nitrate and 0.5g ammonium tungstate are added. The pH of the solution is adjusted to 4. Then 10g carrier is impregnated with the solution, aged for 12 hours, dried at 120°C, and calcinated at 400°C for 4 hours, thereby obtaining the catalyst.

Comparative Example 3

140ml water is added to 300g pseudo-boehmite alumina powder. After kneading and extruding, the formed alumina carrier is dried in air at 120°C, and calcinated at 1030°C for 4 hours, thereby obtaining the Al_2O_3 carrier.

7.9g nickel nitrate is added to 20ml water with stirring. While stirring, 0.6g ammonium molybdate is added. The pH of the solution is adjusted to 4. Then 10g carrier is impregnated with the solution, aged for 12 hours, dried at 120°C, and calcinated at 400°C for 4 hours, thereby obtaining the catalyst.

Example 4

140ml water, 5ml nitric acid (the content of which is 60%) and 12ml silica sol (comprising 40% silica) are added to 300g pseudo-boehmite alumina powder. After kneading and extruding, the formed alumina carrier is dried in air at 120°C, and then calcinated at 460°C for 4 hours. 100g calcinated carrier is impregnated with a solution formed by dissolving 5.8g strontium nitrate into water, dried in air at 120°C, and calcinated at 1020°C for 4 hours, thereby obtaining the Al_2O_3 carrier.

9.5g nickel nitrate is added to 20ml water with stirring. While stirring, 1.1g cerium nitrate, 1.1g lanthanum nitrate and 0.6g potassium chromate are added. The pH of the solution is adjusted to 4. Then 10g carrier is impregnated with the solution, aged for 12 hours, dried at 120°C, and calcinated at 350°C for 4 hours, thereby obtaining the catalyst.

Comparative Example 4

140ml water, 5ml nitric acid (the content of which is 60%) and 12ml silica sol (comprising 40% silica) are added to 300g pseudo-boehmite alumina powder. After kneading and extruding, the formed alumina carrier is dried in air at 120°C, and then calcinated at 460°C for 4 hours. 100g calcinated carrier is impregnated with a solution formed by dissolving 21.6g magnesium nitrate into water, dried in air at 120°C, and calcinated at 1020°C for 4 hours, thereby obtaining the Al_2O_3 carrier.

9.5g nickel nitrate is added to 20ml water with stirring. While stirring, 1.1g cerium nitrate is added. The pH of the solution is adjusted to 4. Then 10g carrier is

impregnated with the solution, aged for 12 hours, dried at 120°C, and calcinated at 350°C for 4 hours, thereby obtaining the catalyst.

Industrial applicability

5 Analysis method:

Distillation range of oil products: measured according to Petroleum Product Testing Method SYB-2110-60;

Iodine value: measured according to IC1 method, expressed in g I₂/100g oil;

10 Diolefin: measured according to maleic anhydride method, expressed in g I₂/100g oil;

Arsenic content: measured by DV-4300 atomic emission spectroscopy;

Sulfur content: measured by WK-2B microcoulometric detector;

Colloid: measured according to Petroleum Product Testing Method SYB-2103-60.

15 The full distillate pyrolysis gasoline is used as the starting materials, the properties of which are shown in Table 1. The catalysts of Examples 1, 2, 3 and 4 as well as Comparative Examples 1, 2, 3 and 4 are evaluated on 100 ml adiabatic bed hydrogenation apparatus. Firstly, the catalyst is reduced under hydrogen at the temperature of 350-400°C for 10 hours. The temperature is lowered to 60°C. After the catalyst is inactivated by cyclohexane containing 1000ppm dimethyl disulfide for 2 hours, the raw oil is added.

Reaction condition:

Reaction pressure: 2.8 MPa,

Intake temperature: room temperature ~60°C,

25 Air speed of fresh raw oil: 3.5h⁻¹,

The volume ratio of hydrogen to oil: 200:1 (based on the fresh oil).

The evaluation is carried out for 200 hours. And the iodine value and diolefin of the products are analyzed every 6 hours. The average data of the iodine value and diolefin of the product for each catalyst during the 200-hour evaluation are shown in Table 2.

Table 1 Indexes of hydrogenation raw oil (C₅-C₉)

Color	Iodine value ×10 ⁻² (g/g)	Diolefin ×10 ⁻² (g/g)	Distillation range (°C)	Sulfur content (ppm)	Colloid ×10 ⁻² (mg/ml)	Density (g/ml)	Arsenic content (ppb)
Yellow	89.2	38.5	45-205	96	6.0	0.815	<20

Table 2 Catalyst composition and average data of 200-hour evaluation in every example and comparative example

Catalyst Index	Example 1	Comparative Example 1	Example 2	Comparative Example 2	Example 3	Comparative Example 3	Example 4	Comparative example 4
Product diolefin ×10 ⁻² (g/g)	1.0	1.18	0.8	1.82	0.9	1.18	0.95	1.15
Product iodine value ×10 ⁻² (g/g)	41.3	44.2	39.8	45.3	40.2	42.6	40.5	41.8
The colloid content after	6.1	5.9	5.8	7.5	6.2	8.6	6.5	6.8

200 hours reaction %									
Specific surface area of the catalyst /m ² ·g ⁻¹		93.78	88.02	105.3	108.9	88.26	87.29	95.84	104.93
Specific pore volume of the catalyst/cm ³ ·g ⁻¹		0.42	0.48	0.46	0.43	0.52	0.45	0.44	0.46
Active component and aids content /wt%	Nickel oxide	18.8	18.8	16.6	16.6	15.6	16.1	17.9	18.9
	Silica	4.3	/	3.7	3.7	2.4	/	3.2	3.2
	Lanthanum oxide	/	/	4.2	4.2	1.8	/	3.0	/
	Cerium oxide	6.1	6.1	/	/	1.9	/	3.2	3.4
	Magnesium oxide	3.9	2.4	2.9	/	2.4	/	/	3.3
	Strontium oxide	/	1.6	1.8	/	/	/	3.2	/
	Molybdenum oxide	1.7	1.7	/	/	/	3.9	/	/
	Tungsten oxide	/	/	3.8	3.8	3.3	/	/	/
	Chromium oxide	/	/	/	/	/	/	2.3	/

1000-hour long period evaluation is performed on the catalyst of Example 2. The evaluation was carried out on 100 ml adiabatic bed hydrogenation apparatus. Firstly, the catalyst is reduced under hydrogen at the temperature of 400-450°C for 10 hours. The temperature is lowered to 60°C. After the catalyst is inactivated by cyclohexane containing 1000ppm dimethyl disulfide for 3 hours, the raw oil is added.

Reaction condition:

Reaction pressure: 2.8 MPa,

Intake temperature: room temperature ~70°C,

Air speed of fresh raw oil: 2.8h⁻¹,

The volume ratio of hydrogen to oil: 200:1 (based on the fresh oil).

The iodine value and diolefin of the product are analyzed every 12 hours. The average data during every 200 hours are taken. The indexes of hydrogenation raw oil (C₅-C₉) are shown in Table 3.

Table 3 Indexes of hydrogenation raw oil (C₅-C₉)

Color	Iodine value ×10 ⁻² (g/g)	Diolefin ×10 ⁻² (g/g)	Distillation range (°C)	Sulfur content (ppm)	Colloid ×10 ⁻² (mg/ml)	Density (g/ml)	Arsenic content (ppb)
Yellow	88.5	39.5	45-205	86	7	0.815	26

The results of evaluation are shown in Table 4. During the 1000-hour operation, the iodine value and diolefin value of the hydrogenation product remain at low level, which sufficiently indicates that the catalyst in Example 2 has good stability and hydrogenation activity.

Table 4 1000-hour evaluation data for catalysts of Example 2 and Comparative Example 3

Cumulative operation time (h)	Hydrogenation product index			
	Catalyst of Example 2		Catalyst of Comparative Example 3	
	Diolefin×10 ⁻²	Iodine	Diolefin×10 ⁻²	Iodine

	(g/g)	value $\times 10^{-2}$ (g/g)	(g/g)	value $\times 10^{-2}$ (g/g)
200	0.8	36.8	0.8	36.0
400	0.8	37.2	1.1	38.9
600	1.0	38.6	1.4	39.8
800	1.2	39.6	1.8	40.3
1000	1.4	40.2	2.5	43.6

In summary, the hydrogenation catalyst according to the present invention has good hydrogenation performance, especially has impurity and colloid resistance as well as good hydrogenation stability. The catalyst can be applied to selective hydrogenation of diolefin unsaturated hydrocarbons, especially the first-stage selective hydrogenation process of full distillate pyrolysis gasoline.

What is claimed is:

1. A selective nickel-based hydrogenation catalyst, with alumina as carrier, characterized in that based on the total weight of the catalyst, it comprises:
 - 14-20% nickel oxide as active component;
 - 1-8% lanthanum oxide and/or cerium oxide;
 - 1-8% VIB group element oxide as aids;
 - 2-8% silica;
 - 1-8% alkaline earth metal oxide;
 wherein said catalyst has a specific surface area of 60-150 m²/g and a pore volume of 0.4-0.6 ml/g.
2. The selective nickel-based hydrogenation catalyst according to claim 1, characterized in that the nickel oxide in the catalyst is in the amount of 15-19%.
3. The selective nickel-based hydrogenation catalyst according to claim 1, characterized in that the lanthanum oxide and/or cerium oxide in the catalyst is in the amount of 3-5%.
4. The selective nickel-based hydrogenation catalyst according to claim 1, characterized in that said alkaline earth metal is magnesium and/or strontium.
5. The selective nickel-based hydrogenation catalyst according to claim 1, characterized in that the alkaline earth metal oxide in the catalyst is in the amount of 2-5%.
6. The selective nickel-based hydrogenation catalyst according to claim 1, characterized in that said VIB group element is one or more of chromium, molybdenum and tungsten.
7. The selective nickel-based hydrogenation catalyst according to claim 1, characterized in that the VIB group element oxide in the catalyst is in the amount of 3-6%.
8. A method for preparing the selective nickel-based hydrogenation catalyst according to claim 1, comprising:
 - adding silica or its precursor and alkaline earth metal oxide or its precursor into alumina carrier;
 - calcinating at the temperature of 800-1100°C for 3-6 hours to form the modified alumina carrier;
 - adding the soluble salts of nickel, rare earth element and VIB group element into water, wherein the rare earth element is lanthanum and/or cerium;
 - after fully dissolution, adjusting the pH of the solution to 4-5 to form an impregnating solution;
 - impregnating the modified alumina carrier with the impregnating solution;
 - drying at the temperature of 40-120°C; and
 - calcinating at the temperature of 350-450°C for 3-6 hours, thereby obtaining the resultant catalyst.

9. The method according to claim 8, characterized in that the modified alumina carrier is prepared by:

- 5 adding silica sol, nitric acid and water into alumina hydrate;
- after kneading and extruding, drying at the temperature of 40-120°C;
- calcinating at the temperature of 300-600°C for 4-6 hours;
- impregnating the formed carrier with the impregnating solution formed by adding the alkaline earth metal oxide into water;
- drying at the temperature of 40-120°C; and
- 10 calcinating at the temperature of 800-1100°C for 4-6 hours, thereby forming the modified alumina carrier.