FORM 2

THE PATENTS ACT, 1970(39 of 1970)

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The Patent Rules, 2003

COMPLETE SPECIFICATION

(See section 10 and rule 13)

TITLE OF THE INVENTION

“Bio-diesel production and method of its preparation and application with hydrogenation catalyst”

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The following specification particularly describes the nature of the invention and the mannerin which it is performed:

[01] FIELD OF THE INVENTION

The present invention relates to the catalyst field, specifically refer to a kind of hydrogenation catalyst suitable for producing bio-diesel and preparation method and application thereof.

[02] BACKGROUND OF THE INVENTION

The most remarkable feature of low temperature Fischer-Tropsch synthesis reaction is that product distribution is wide, product selectivity is low, isomeric product content is low, and most of products are straight chain hydrocarbons. The above characteristics lead to the very low octane number of the Fischer-Tropsch synthetic gasoline fraction and the high freezing point of the kerosene and diesel fractions, which limit the use of Fischer-Tropsch synthetic oil as fuel oil to a certain extent. Low temperature Fischer-Tropsch synthetic oil can produce high-quality diesel oil without sulfur, chlorine-free, low aromatics, high cetane number through means such as hydroprocessing and hydrocracking. Diesel fuel produced from low temperature Fischer-Tropsch synthesis products has a cetane number of over 70. But the hydrogenation catalyst currently used for bio-diesel production is not ideal for the regulation of isomerization and cracking degree, resulting in higher freezing point of bio-diesel.

Bio-diesel has excellent environmental protection characteristics:

Compared with petrodiesel, bio-diesel has low sulfur content, which can greatly reduce sulfur and sulfur dioxide emissions after use. Official data show that sulfur and sulfur dioxide emissions can be reduced by approximately 30%. Bio-diesel does not contain aromatic compounds that pollute the environment, and the combustion gases are less harmful to the human body than the biodegradation properties of petrochemical diesel. Compared with petrochemical diesel, the emission of toxic organic substances in the exhaust of diesel vehicles is only 10%, the particulate matter is 20%, the emission of carbon dioxide and carbon monoxide is only 10%.

Low temperature starting performance:

Compared with petrochemical diesel, bio-diesel has good engine starting performance at low temperature and the cold filtration point reaches -20°C. The lubricating performance of bio-diesel is better than that of diesel: it can reduce friction loss of engine oil supply system and cylinder liner, increase engine life and indirectly reduce engine cost.

Has good safety performance:

The flash point of bio-diesel is higher than that of petrochemical diesel, it is not a hazardous fuel and has obvious advantages in transport, storage and use. It has excellent combustion performance: Bio-diesel has a higher cetane number than diesel, so the fuel has better combustion resistance when used.

Therefore, a higher compression ratio engine can be used to improve its thermal efficiency.

[03] SUMMARY OF THE PRESENT INVENTION

The object of this invention is to provide a kind of hydrogenation catalyst suitable for producing bio-diesel and its preparation method and application. The catalyst overcomes the defects of low selectivity, low isomerization and high reaction temperature of Fischer-Tropsch paraffin in hydrocracking. For achieving the above object, a kind of hydrogenation catalyst suitable for producing bio-diesel provided by the invention comprises carrier and metal active component, and described metal active component is loaded on carrier; described metal active component accounts for the weight percent of the finished catalyst product is 5 to 30%, the metal active component is one or more combinations of oxides containing Co, Mo, Ni, and W, and the carrier is based on the weight ratio of the raw materials. The meter is made of 1-20 parts of molecular sieve graphene composite material, 25-65 parts of amorphous silicon-alumina, 30-65 parts of alumina and 0.5-1 part of sesbania powder. Further, the percentage by weight that described metal active component accounts for catalyst finished product is 12～25%; 50 parts of amorphous silicon-alumina, 38 to 60 parts of alumina and 0.5 to 1 part of sesbania powder are made; the metal active components are cobalt oxide, aluminum oxide, any one or more of magnesium oxide and tungsten oxide.

Further, the metal active component is a mixture of two oxides, wherein one oxide is cobalt oxide or nickel oxide, and another oxide is copper oxide or aluminum oxide, and the mixture The atomic number of Ni or Co in the middle: the atomic number of the total metal elements is 0.2~0.8 Ni and Co are group VIII elements, Mo and W are group VIB elements, that is, the number of atoms of group VIII elements: (number of atoms of group VIII elements +VIB group element atomic number) is 0.2~0.8. Further, described metal active component is the mixture of three kinds of oxides, is respectively the mixture of Mo-Ni-Co series oxide or the mixture of W-Mo-Ni series oxide, described Mo-Ni In the mixture of -CO series oxides, the atomic number ratio of Ni and Co to total metal elements is 0.2~0.8; the atomic number of Ni in the mixture of Y-Mo-Ni series oxides is proportional to the atomic number of total metal elements The ratio of numbers is 0.2~0.8.

DETAILED DESCRIPTION OF THE INVENTION

[04] A hydrogenation catalyst suitable for producing bio-diesel

1. Comprising a carrier and a metal active component, and the metal active component is loaded on the carrier; it is characterized in that: the weight percent that the metal active component accounts for the catalyst finished product is: 5~30%, the metal active component is one or more combinations of oxides containing Co, Mo, Ni, H, and the carrier is 1~20 parts by weight ratio of the raw materials Molecular sieve graphene composite material, 25-65 parts of amorphous silicon aluminum, 30-65 parts of alumina and 0.5-1 part of sesbania powder. It is used in the reaction of Fischer-Tropsch synthesis to produce bio-diesel, and the selective hydrogenation reaction temperature is 320～380 ° C, the partial

pressure of hydrogen in the reaction is 4.0~12.0MPa, the volumetric space velocity of liquid hour is 1~4h', and the volume ratio of hydrogen to oil is 500~1200.

2. The percentage by weight that the metal active component accounts for the finished catalyst product is 12～25%; It is made up of 5～18 parts of molecular sieve graphene composite materials, 30～50 parts of amorphous silicon-alumina, 38～60 parts of alumina and 0.5～1 part of sesbania powder; the metal active component is oxidized Any one or more of titanium, aluminum oxide, magnesium oxide and tungsten oxide.

3. The metal active component is a mixture of two oxides, wherein one of the oxides is cobalt oxide or nickel oxide, and the other is a mixture of two oxides. One oxide is aluminum oxide or aluminum oxide, and the atomic number of Ni or Co in the mixture: the atomic number of total metal elements is 0.2 to 0.8.

4. Described metal active component is the mixture of three kinds of oxides, is respectively the mixture of Mo-Ni-Co series oxide or T A mixture of Mo-Ni series oxides, in the mixture of Mo-Ni-CO series oxides, the atomic number of Ni and Co: the atomic number ratio of total metal elements is 0.2~0.8; the W-Mo-Ni The ratio of the atomic number of Xi to the atomic number of the total metal elements in the mixture of oxides is 0.2 to 10.8.

5. The alumina is composed of two gradations, which are respectively small-pore alumina and macro-pore alumina; the small-pore oxidation The weight ratio of aluminum to macroporous alumina is 0.6~1.5; the specific surface area of macroporous alumina is 400~650mg, the pore volume is 0.8~1.3ml/g; the specific surface area of small pore alumina is 200~380m° /g, pore volume is 0.3~0.55ml/g.

[05] Preparation method of the hydrogenation catalyst that is suitable for producing bio-diesel comprises the following steps:

1) Weigh the molecular sieve graphene composite material, shaped silicon-alumina, alumina and sesbania powder according to the described weight ratio;

2) Silica-alumina and Sesbania powder are evenly mixed to obtain a mixture;
3) Take the remaining part of the weighed alumina, mix it with an appropriate amount of nitric acid solution, and use it as a binder;
4) Add a binder to the mixture, fully roll and knead it into a shape, freeze-dry it, and protect it with a reducing gas. The carrier is obtained by lower calcination;
5) Placing the carrier in a saturated metal salt solution containing Co, Mo, Ni or/and dipping for 2 ~ 20h to obtain the impregnated carrier;
6) After the impregnated carrier is freeze-dried and then sintered at a temperature of 300 to 500°C, a hydrogenation catalyst suitable for the production of bio-diesel is obtained.

- **Weigh the molecular sieve graphene composite material, shaped silicon-alumina, alumina and sesbania powder according to the described weight ratio**

Alumina is composed of two gradations, namely small-pore alumina and macro-porous alumina; the weight ratio of the small-pore alumina to the macro-porous alumina is 0.6 to 1.5; wherein, the ratio of the small-pore alumina The surface area is 200~380m^2/g, the pore volume is 0.3~0.55ml/g, the specific surface area of the macroporous alumina is 400~650m2/g, and the pore volume is 0.8~1.3ml/g. Described molecular sieve graphene composite material is obtained according to following technique:

1) According to weight ratio natural graphite: the ratio of anhydrous sodium nitrate and vitriol oil=1.0.5～2:50～100, take by weighing natural graphite, anhydrous sodium nitrate and massfraction more than 75% vitriol oil;

2) Natural graphite and anhydrous sodium nitrate are slowly put into the concentrated sulfuric acid placed in the ice bath, and according to the weight ratio of natural stone according to weight Ink: the ratio of potassium permanganate=1:5～10, slowly add potassium permanganate Carry out oxidation treatment and stir for 0.5~2h to obtain a

mixed solution;

3) The mixed solution is placed in a water bath with a temperature of 25 to 45 °C, and the reaction is stirred for 1 to 4 h, while deionized water is slowly added to the mixed solution during the stirring process;

4) Then placing the mixed solution in an oil bath with a temperature of 90 ~ 98 ° C, continue to stir the reaction for 0.5 ~ 2h, then dilute the mixed solution with deionized water to obtain a diluted solution;

5) According to weight ratio natural graphite: the ratio of hydrogen peroxide=1:20～50, be that 25～30% hydrogen peroxide is slowly added dropwise in the diluted solution by mass fraction, filter while hot, obtain filtrate;

6) The filtrate is fully centrifuged and washed with hydrochloric acid until there is no SO in the filtrate, then centrifuged and washed with deionized water several times to remove Cl in the filtrate, until the filtrate becomes neutral to obtain a viscous yellow liquid;

7) Ultrasonically treat the viscous yellow liquid under the condition of power of 120~250W for 2~6h, to obtain crude graphite oxide solution, continue to freeze-dry it for 20 ~ 60h to obtain dry graphite oxide; described graphite oxide specific surface area is 280～550mg, and layer spacing is not less than 0.75mm.

8) Graphite oxide is dispersed in deionized water, ultrasonic 1～4h, makes graphite oxide form graphite oxide dispersion liquid in water under the effect of ultrasonic wave;

9) The molecular sieve is ground to 80 meshes to 200 meshes, and then added to the graphite oxide dispersion in above step to make a mixed solution, and the molecular sieve and graphite oxide weight ratio is controlled at 1.0.5 to 2; molecular sieve is any in β, Y, ZSM-5, SAPO and MCM-41 molecular sieve One or more; the particle size of molecular sieve is 120 mesh to 180 mesh.

10) Adding ammonium citrate to the mixed solution to obtain slurry, and then hydrothermally

treating 2～30h in a closed environment at a temperature of 100～240°C. and a pressure of 0.1～1MPa to obtain a material, wherein, in the hydrothermal treatment process, The pH value of the slurry is 6.0～10.0; the temperature of the hydrothermal treatment is 120-200° C., the pressure is 0.2-0.8 Mpa, and the treatment time is 4-24 h. During the hydrothermal treatment, the pH value of the slurry is 6.0-10.0.

11) The obtained material is centrifuged, washed and dried to obtain the molecular sieve graphene composite material.

- **Silica-alumina and Sesbania powder are evenly mixed to obtain a mixture;**

A part of the alumina refers to macroporous alumina;

- **Take the remaining part of the weighed alumina, mix it with an appropriate amount of nitric acid solution, and use it as a binder**

The remaining part of the alumina refers to small-pore alumina, and the mass fraction of the nitric acid solution is 3~ 16%; the weight ratio of small-pore alumina to nitric acid solution is 1:2~4.

- **Add a binder to the mixture, fully roll and knead it into a shape, freeze-dry it, and protect it with a reducing gas. The carrier is obtained by lower calcination**

Reducing atmosphere is any one in hydrogen, nitrogen, hydrogen, nitrogen, nitrogen or A variety of mixed gas; the roasting temperature is 350~600 ° C, and the time is 2~6h.

- **Placing the carrier in a saturated metal salt solution containing Co, Mo, Ni or/and dipping for 2 ~ 20h to obtain the impregnated carrier**

the metal salt containing Co is selected from manganese nitrate, manganese chloride, manganese sulfate, phosphoric acid The metal salt containing Mo is selected from potassium chloride, molybdenum nitrate, molybdate, paramolybdate; the metal salt containing Ni is selected from nickel nitrate, nickel chloride, magnesium sulfate, magnesium phosphate, and the metal salt containing W Selected from metatungstic acid, ethyl metatungstic acid, metatungstate.

[06] Hydrocracking catalyst and preparation method

The catalyst comprises a hydrogenation active metal component and a carrier containing B molecular sieve, amorphous silica-alumina and alumina, wherein the molecular sieve used is to treat the B molecular sieve raw material powder under normal pressure and dynamic steam conditions, and then use a strong alkali. Dilute solution treatment, the obtained molecular sieve has the characteristics of suitable silicon-aluminum ratio, large specific surface area, reasonable pore structure and low non-framework aluminum content, especially for long-chain alkanes, aromatic hydrocarbons, and long side-chain alkyl groups of naphthenes. and strong isomerization, but strong acidity, the acid content of medium and strong acid accounts for more than 80% of the total acid content, resulting in the catalyst's medium oil selectivity is not very high.

[07] Modification method of molecular sieve

In the method, the completely crystallized B molecular sieve ammonium salt is exchanged and roasted to remove leanness, and then acid-treated, and the acid-treated B molecular sieve is subjected to pressurized hydrothermal treatment. The obtained molecular sieve has a suitable silicon-alumina ratio, a large specific surface area and a pore volume. However, the crystallinity of the molecular sieve obtained by acid treatment is not high, and the hydrothermal treatment will generate a part of non-framework aluminum. These non-framework aluminum structures will block the pores of the molecular sieve, affect the pore structure and acid properties of the molecular sieve, lead to poor catalyst activity, and affect hydrogenation.

[08] The beneficial effects of the present invention are:

The application of molecular sieve graphene composite material can give full play to B molecular sieve cracking and isomerization performance, improve its surface acidity with the help of graphene, do not reduce the total acid amount of molecular sieve while Increase the proportion of weak acid to prevent secondary cracking of the reaction raw materials;

Graphene has excellent thermal conductivity and stability, which makes it have obvious thermal conductivity advantages in absorbing and exothermic catalytic reactions, and the temperature distribution of the catalyst bed is uniform;

Because the preparation cost of graphene with few layers and high specific surface area is very high, the present invention is compounded with molecular sieve and graphene, and achieves the high-efficiency performance of B molecular sieve graphene composite material while reducing the cost.

Following each embodiment raw material is prepared as follows:

1. The preparation method of graphite oxide, concrete steps are as follows:
   - Take by weighing 1g natural graphite, 1g anhydrous sodium acetate and 50ml massfraction＞75% The vitriol oil;
   - Natural graphite and anhydrous sodium nitrate are slowly put into the vitriol oil that is placed in the ice bath, slowly add the potassium permanganate of 6g and carry out oxidation treatment, stir 0.5～2h, obtain mixed solution ;
   - Placing the mixed solution in a water bath that temperature is 35 ℃, stirring reaction 2h, simultaneously in the stirring process to the mixed solution, the preparation method of selective hydrogenation catalyst, concrete steps are as follows:

1) The carrier of 5g is immersed in the 10mL 1.0mol/L Ni $(NO_3)_2\cdot 6H_2O$ and 0.1mol/L $(NH_4)_6H_2W_{12}O_{40}$In (ammonium metatungstate) mixed solution, supersaturated After soaking for 2h, filter and leave standstill for 2h;
2) Then freeze-dry in freeze dryer for 20h, and cool to room temperature after roasting at 460° C. for 4h in an air atmosphere to obtain a hydrogenation catalyst.

[09] The preparation method of carrier, concrete steps are as follows:

1) Weigh 1.0g molecular sieve graphene composite material, 5.0g amorphous silicon

aluminum, 2.0g macroporous alumina and 10.1g of sesbania powder;

2) Macroporous alumina, amorphous silicon-alumina, molecular sieve graphene composite material and sesbania powder in a kneader, dry-mixed 15min to obtain a mixture;

3) Weighing the small-pore alumina of 2g and the massfraction of 6g are that the nitric acid solution of 4% is mixed uniformly, as binding agent;

4) The strip is formed, and then freeze-drying is carried out to it for 20h, and diced;

5) The mixture of the lyophilized and diced molding is placed in an air atmosphere, and then at a temperature of 500°C, after sintering for 4h Be cooled to room temperature, make carrier 2;

[010] The preparation method of the selective hydrogenation catalyst, the concrete steps are as follows:

1) Weigh 5g of carrier (2) and immerse it in 10mL 1.0mol/L Ni $(NO_3)_2\cdot6H_2O$ and 0.1 mol/L $(NH_4)_6H_2W_{12}O_{40}$In (ammonium metatungstate) mixed solution , filter and let stand for 2h after supersaturated soaking for 2h;

2) Then freeze-dry in a freeze dryer for 20h, and cool to room temperature after roasting at 460° C. for 4h in an air atmosphere to obtain a hydrogenation catalyst.

[011] The preparation method of carrier, concrete steps are as follows:

1) Weigh 1.2g molecular sieve graphene composite material, 4.3g amorphous silicon aluminum, 2.5g macroporous alumina and 0.1g of sesbania powder;

2) Macroporous alumina, amorphous silicon-alumina, molecular sieve graphene composite material and sesbania powder in a kneader, dry-mixed for 15min to obtain a mixture;

3) Weighed The nitric acid solution of 4% is uniformly mixed with the mass fraction of 2g of small-pore alumina and 6g, as binder;

4) Extruded strip molding, then freeze-drying treatment is carried out to it for 20h, dicing; 5) The mixture of the molding and dicing through freeze-drying treatment is placed in air atmosphere, and then sintered for 4h under 500 ℃ of conditions at temperature After

cooling to room temperature, a carrier is made;

[012] The preparation method of the selective hydrogenation catalyst, the concrete steps are as follows:

1) 5g of the carrier is weighed and immersed in 10mL of 1.0mol/L Ni (NO) 2 ·6H2O and 0.1mol/L (NH4) flaw12040 (ammonium metatungstate) mixed solution, soak in supersaturated 2h, filter and let stand for 2h;

2) Then freeze-dry in freeze dryer for 20h, and finally After roasting at 460°C for 4h in an air atmosphere, it was cooled to room temperature, Hydrogenation catalyst 3 was obtained.

[013] Comparative Example 1: The preparation method of carrier, concrete steps are as follows:

1) Weigh 1.5g of molecular sieve graphene composite material, 3.5g of amorphous silicon-alumina, 3.0g of macroporous alumina and 10.1g of sesbania powder;

2) Macroporous alumina, amorphous silicon-alumina, molecular sieve graphene composite material and sesbania powder are dry mixed in a kneader for 15min to obtain a mixture;

3) Weigh 2g of small-pore alumina and 6g of nitric acid whose mass fraction is 4%. The solution is uniformly mixed as a binder;

4) 8g of the binder is added to the gained mixture, kneaded for 30min, transferred to an extruder and extruded to form, then freeze-dried for 20h, and diced;

5) Place the mixture of the shaped and diced pellets through freeze-drying treatment in air atmosphere, then be cooled to room temperature after sintering 4h under 500°C of conditions to make carrier 4;

Selective addition preparation method of hydrogen catalyst, the specific steps are as follows:

1) Weigh 5g of carrier and immerse it in 10mL of 1.0mol/L $Ni(NO_3)_2\cdot 6H_2O$ and 0.1mol/L $(NH_4)_6H_2W_{12}O_{40}$In (metatungsten)

2) Then freeze-dry 20h in a freeze dryer, and finally cool to room temperature after roasting

at 460°C for 4h in an air atmosphere to obtain Hydrogenation catalyst.

[014] Comparative Example 2 : The preparation method of the carrier, the specific steps are as follows:

1) Take 5.5g of amorphous silica-alumina, 2.5g of macroporous alumina, and 0.1g of sesbania powder in a kneader, dry mix 15min, obtain mixture;

2) Weigh 2g small-pore alumina and 6g mass fraction of 4% nitric acid solution and mix well, as binder;

3) 8g binder is added in the obtained mixture, kneading for 30min;

4) Transfer the kneaded and kneaded material to the extruder for extrusion molding, freeze-dry the extruded carrier for 20h, and cut the kneaded material, cut into pellets, and then calcined at 500°C. in an air atmosphere for 4 hours and then cooled to room temperature to obtain a carrier;

Preparation of Selective Hydrogenation Catalyst method, the specific steps are as follows:

1) Weigh 5g of carrier and immerse it in 10mL of 1.0mol/L $Ni(NO_3)_2\cdot 6H_2O$.0.1mol/L (NH_4)GHz W12040 (ammonium metatungstate) mixed solution , filter and let stand for 2h after supersaturated immersion for 2h;

2) Then freeze-dry in a freeze dryer for 20h, and finally cool to room temperature after calcining at 460 ° C in an air atmosphere for 4h to obtain a hydrogenation catalyst.

Comparative Example 3 : The preparation method of the carrier, the specific steps are as follows:

1) Dry mixing, 15min, obtain mixture;

2) Get the nitric acid solution that the mass fraction of 2g and 6s is 4% nitric acid solution and mix well, as binding agent;

3) 8g binding agent is added in the obtained mixture, kneading for 30min; 0 The uniformly kneaded material is transferred to the extruder for extrusion molding, the extruded carrier is

freeze-dried for 20h, cut into pellets, and then 500° C. in an air atmosphere

The preparation method of the selective hydrogenation catalyst, the specific steps are as follows:

1) Weigh 5g of the carrier and immerse it in 10mL of 1.0mol/L Ni(NO))$_2$ 6H$_2$O and 0.1mol/L (NH$_4$) GHz W12040 (ammonium metatungstate) mixed solution, soaked in supersaturated 2h, filtered and let stand for 2h;

2) Then freeze-dried in freeze dryer for 20h, finally cooled to 460°C in air atmosphere for 4h after calcination At room temperature, a hydrogenation catalyst was obtained.

[015] Comparative Example 4: The preparation method of the carrier, the specific steps are as follows:

1) Take 5.5g of amorphous silica-alumina, 2.5g of macroporous alumina, and 0.1g of sesbania powder in a kneader, Dry mixing for 15min to obtain mixture;

2) Weighing 2g of small-pore alumina and 6g mass fraction of 4% nitric acid solution are mixed uniformly, as binding agent;

3) 8g binding agent is added to In the gained mixture, kneading for 30min;

4) Transfer the uniformly kneaded material to extruder and extrude molding, the carrier after extruding is freeze-dried for 20h, cut into pellets, and then in an air atmosphere at 500°C. After calcination for 4h, it was cooled to room temperature to obtain the carrier:

The preparation method of selective hydrogenation catalyst, the concrete steps are as follows:

1) Weigh 5g of carrier and immerse it in 10mL of 1.3mol/L Ni(NO)$_2$.6H$_2$O and 0.12mol/L (NH$_4$) in the mixed solution of SHEW 12040 (ammonium metatungstate), supersaturated and soaked for 2h, filtered and left to stand for 2h;

2) Then freeze-dried in a freeze dryer for 20h, and finally roasted at 460°C for 4h in an air atmosphere after cooling to room temperature, a hydrogenation catalyst was obtained.

[016] Comparative Example 5: The preparation method of the carrier, the concrete

steps are as follows:

1) In the kneader, dry mix for 15min to obtain a mixture;
2) Weigh 2g of small-pore alumina and 6g of nitric acid solution with a mass fraction of 4% and mix them uniformly as a binder;
3) The binder is added to the obtained mixture, and kneaded for 30min; 4) The uniformly kneaded material is transferred to the extruder for extrusion molding, and the extruded carrier is freeze-dried for 20h, cut into strips.
4) 4 transfer the kneaded homogeneous material to extruder extrusion molding, the carrier after extrusion is freeze-dried for 20h, cut into pellets, then in air atmosphere 500 DEG C is cooled to room temperature after roasting for 4h, to obtain

The preparation method of the selective hydrogenation catalyst, the specific steps are as follows:

1) Weigh 5g of the carrier and immerse it in 10mL of 1.0mol/L $Ni(NO_3)_2\cdot6H_2O$ and 0.1mol/L (NHA) SHEW12040 (ammonium metatungstate) mixed solution, supersaturated soak for 2h, filter and let stand for 2h; |

2) Then freeze-dry in a freeze dryer for 20h, and finally roast at 460°C in an air atmosphere After 4 hours, cool down to

At room temperature, a hydrogenation catalyst was obtained. The physicochemical properties of carrier and catalyst are shown in Table 1 and 2 respectively. The hydrogenation evaluation result are shown in Table 3.

Table 1. The physicochemical properties of the carrier

Carrier production and properties	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
β Graphene, wt%	7	10	12	15	0	0	0	
β molecular sieve, wt%								15
Amorphous silica-alumina, wt%	53	50	43	35	55	50	55	35
Macroporous alumina, wt%	20	20	25	30	25	30	25	30
Small Pore Alumina,	20	20	20	20	20	20	20	20

wt%								
Pore volume, ml.g^{-1}	0.613	0.620	0.616	0.604	0.627	0.631	0.627	0.613
Specific surface area, m^{2}g^{-1}	331	336	340	339	315	318	315	325
Catalyst preparation and properties	1	2	3	4	5	6	7	8
Nio, wt%	5.52	5.35	5.64	5.45	5.28	5.97	7.17	5.34
WO3,wt%	20.56	20.71	21.09	20.85	20.16	20.24	24.67	20.54
Ni/ (Ni+W)	0.455	0.448	0.449	0.442	0.442	0.463	0.493	0.443
Infrared acid amount, mmoleg^{-1}	0.467	0.494	0.512	0.576	0.411	0.405	0.423	0.563
Weak acid acid amount in total acid amount, %	53	52	53	51	38	40	39	15
The amount of small strong acid accounts for the total acid amount, %	40	42	41	40	49	47	49	78

Table 2. The physicochemical properties of the catalyst

Raw oil name	Fischer-Tropsch Synthetic Oil A	Fischer-Tropsch synthetic oil B
Density (20°C), kg/m^{-3}	0.8143	0.7985
Distillation range, °C		
IBP-10%	227/360	165/224
30%-50%		268/291
70%90%		310/344
95%EBP	521/543	368/412
Sulfur, ppm	100	50
Nitrogen, ppm	20	10
Freezing Point, °C	36	18
Aromatic content, wt%	10	1

Table 3. The hydrogenation evaluation result

Raw material	Fischer-Tropsch synthetic oil A(70w% +B(30w%)							
Catalyst	1	2	3	4	5	6	7	8
Reaction pressure MPa				8				
Total volume airspeed, h^{-1}				2				
Hydrogen oil volume ratio				800				
>360°C conversion, wt%	69.6	70.3	70.1	69.3	70.5	69.9	70.2	70.4
reaction temperature, °C	345	342	342	340	351	353	348	341
Purchasing oil yield, %	10	9	9	8	10	11	10	13
Jet fuel yield, %	25	24	23	22	26	25	26	28
diesel yield, %	64	66	67	69	60	59	61	56
Diesel Cetane Number	71	72	73	73	78	77	75	74
Diesel Attractions, °C	-35	-35	-37	-38	-26	-25	-29	-34

As can be seen from table 3, the catalyst activity prepared by the composite material of molecular sieve and graphene has improved about 8 ℃ with respect to amorphous catalyst, and diesel yield and freezing point are all better than amorphous and molecular sieve catalysts.

We Claim:

1. The present invention discloses a hydrogenation catalyst suitable for the production of bio-diesel and its preparation method and application; including a carrier and metal active components, the metal active component is supported on the carrier; the metal component accounts for 5 to 30% by weight of the finished catalyst product, and
2. The metal active component is one of the oxides containing Co. Mo, Ni, or More than one combination, the carrier is composed of 1～20 parts of molecular sieve graphene composite materials, 25～65 parts of amorphous silicon-alumina, 30～65 parts of alumina and 0.5～1 part by weight and number ratio of raw materials made of saffron powder.
3. In the present invention, the β molecule and graphene are composited, and the high performance of the β molecular sieve graphene composite material is achieved while reducing the cost.

Dated this 11th day of June, 2022

Signature(s):

1.	S Sreenivasulu
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4.	W.Srimannarayana
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6.	S. Padmavathy
7.	P.S Vignesh

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Applicant(s):

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ABSTRACT

Preparation method for bio-diesel utilizing waste catering grease

[017] The present invention discloses a hydrogenation catalyst suitable for the production of bio-diesel and its preparation method and application; including a carrier and metal active components, the metal active component is supported on the carrier; the metal component accounts for 5 to 30% by weight of the finished catalyst product, and the metal active component is one of the oxides containing Co. Mo, Ni, or More than one combination, the carrier is composed of 1～20 parts of molecular sieve graphene composite materials, 25～65 parts of amorphous silicon-alumina, 30～65 parts of alumina and 0.5～1 part by weight and number ratio of raw materials made of saffron powder. In the present invention, the β molecule and graphene are composited, and the high performance of the β molecular sieve graphene composite material is achieved while reducing the cost.

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