

FORM 1

610285

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Shell Internationale Research Maatschappij B.V., a Netherlands Company, of Carel van Bylandtlaan 30, 2596 HR, The Hague, THE NETHERLANDS, hereby apply for the grant of a standard patent for an invention entitled:

Process for the Preparation of Hydrotreating Catalysts from Hydrogels

which is described in the accompanying complete specification.

Details of basic application(s):-

|                          |                 |                          |
|--------------------------|-----------------|--------------------------|
| <u>Basic Applic. No:</u> | <u>Country:</u> | <u>Application Date:</u> |
| 123510                   | US              | 20 November 1987         |

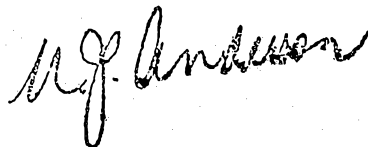
The address for service is:-

**Spruson & Ferguson**  
Patent Attorneys  
Level 33 St Martins Tower  
31 Market Street  
Sydney New South Wales Australia

DATED this SEVENTEENTH day of NOVEMBER 1988

Shell Internationale Research Maatschappij B.V.

By:



Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS

OUR REF: 76119  
S&F CODE: 161750

003692

APPLICATION ACCEPTED AND AMENDMENTS

FILED 27.2.91

5845/10

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA  
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A  
CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

Process for the preparation of hydrotreating catalysts from hydrogels

I, Onno Aalbers, of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands, do solemnly and sincerely declare as follows:-

1. I am authorised by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., the applicant for the patent to make this declaration on its behalf.
2. The basic application(s) as defined by Section 141 of the Act was/were made in the U.S.A.  
on 20th November, 1987  
by RICHARD ALAN KEMP
3. Richard Alan KEMP, a U.S.-citizen of 11510 Chariot, Stafford, Texas 77477, U.S.A.

(respectively), is/are the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The Applicant is the assignee of the actual inventor(s).

4. The basic application(s) referred to in paragraph 2 of this Declaration was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

DECLARED at The Hague this 19th day of September 1988

.....  
Onno Aalbers

TO: THE COMMISSIONER OF PATENTS  
AUSTRALIA

---

**(12) PATENT ABRIDGMENT      (11) Document No. AU-B-25676/88**  
**(19) AUSTRALIAN PATENT OFFICE      (10) Acceptance No. 610285**

---

(54) Title  
**PROCESS FOR THE PREPARATION OF HYDROTREATING CATALYSTS FROM HYDROGELS**

International Patent Classification(s)  
(51)<sup>4</sup> **B01J 037/03      B01J 023/85      B01J 023/88      B01J 035/10**  
**B01J 037/02**

(21) Application No. : **25676/88**      (22) Application Date : **17.11.88**

(30) Priority Data

(31) Number      (32) Date      (33) Country  
**123510      20.11.87      US UNITED STATES OF AMERICA**

(43) Publication Date : **25.05.89**

(44) Publication Date of Accepted Application : **16.05.91**

(71) Applicant(s)  
**SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.**

(72) Inventor(s)  
**RICHARD ALAN KEMP**

(74) Attorney or Agent  
**SPRUSON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001**

(56) Prior Art Documents  
**US 4786404**  
**US 4717705**  
**US 4716140**

(57) Claim

1. A process for preparing highly active catalysts having surface areas of at least 300 m<sup>2</sup>/g and at least 70% of the pore volume in pores having diameters less than 7 nm, which process comprises:

- (a) precipitating an aqueous solution of one or more aluminium salt(s) by adjusting the pH of said solution to a range between 5.5 and 10.0 at a temperature in the range between 20°C and 90°C, thereby forming a precipitate,
- (b) aging the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 8.0 to 12.0,
- (c) washing the precipitate,
- (d) mixing the precipitate with a nickel compound and a heavy metal compound wherein the heavy metal is selected from the group consisting of molybdenum, tungsten, and mixtures thereof, at a pH in the range between 4.0 and 10.0 at a temperature in the range between 25°C and 100°C until adsorption of the nickel and heavy metal compound onto the precipitate is

(11) AU-B-25676/88  
(10) 610285

-2-

sufficient to yield a final catalyst having from 1%w to 6%w nickel and from 8%w to 40%w heavy metal,

(e) extruding the product of step (d), and

(f) drying and calcining the product of step (e) at a temperature ranging from 300°C to 900°C.

19. A catalyst which comprises a catalytically effective amount of nickel and a catalytically effective amount of a heavy metal selected from the group consisting of molybdenum, tungsten or mixtures thereof on a support said catalyst having a surface area of at least 300 m<sup>2</sup>/g and at least 70%w of the pore volume in pores having diameters less than 7 nm and wherein said catalyst has been prepared by a process according to claim 18.

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

610285

(ORIGINAL)

FOR OFFICE USE:

Class      Int Class

Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art:

This document contains the  
amendments made under  
Section 49 and is correct for  
printing.

Name and Address  
of Applicant:

Shell Internationale Research Maatschappij B.V.  
Carel van Bylandtlaan 30  
2596 HR  
The Hague  
THE NETHERLANDS

Address for Service:

Spruson & Ferguson, Patent Attorneys  
Level 33 St Martins Tower, 31 Market Street  
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Process for the Preparation of Hydrotreating Catalysts from  
Hydrogels

The following statement is a full description of this invention, including the  
best method of performing it known to me/us

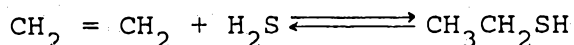
PROCESS FOR THE PREPARATION OF HYDROTREATING  
CATALYSTS FROM HYDROGELS

The present invention relates to a process for preparing highly active alumina hydrogel-derived catalysts.

In the catalytic processing of petroleum  
5 feedstocks, it is often desirable to alter the pore structure of the catalyst in order to accommodate different types of feeds. For example, when processing feedstocks of high metals content, the metals tend to deposit rapidly on the catalyst surface and plug the  
10 pores of conventional hydroprocessing catalysts, resulting in a loss of catalytic activity for sulphur removal. To facilitate the diffusion of large components into and out of the catalyst and to prevent surface deposits of coke and metals, large pore  
15 diameters are required. On the other hand, when processing feedstocks with no metals or with low metals contents, it may be technically and economically desirable to use a narrow-pore catalyst. The catalysts prepared according to the present invention are  
20 narrow-pore catalysts which have high desulphurization and hydrogenation activities.

It is known that in certain hydrocracking operations the hydrocracked products appear to be contaminated with mercaptans, even in cases where the  
25 initial feed placed in the hydrocracking zone is free of mercaptans. There is, therefore, a need to eliminate mercaptans from the hydrocracked products. In addition to being useful for a variety of

hydrotreating applications in which high desulphurization and hydrogenation activities are required, the catalysts prepared in accordance with the present invention are also of particular use in a non-acidic post-treatment for hydrocracked products which are contaminated with mercaptans. These mercaptans are apparently synthesized during or after hydrocracking operations by the reaction of olefins with hydrogen sulphide, as exemplified by the equation:



This reaction is catalyzed by the acidic nature of the hydrocracking catalysts used in the hydrocracking zone. It has been found that the catalysts prepared according to the invention, which have high hydrogenation and desulphurization abilities, prevent the reaction of olefins and hydrogen sulphide to mercaptans by hydrogenating the olefins, or, alternatively, reduce the concentration of the mercaptans which are formed by conventional desulphurization.

The present invention relates to a process for preparing highly active catalysts having surface areas of at least 300 m<sup>2</sup>/g and at least 70% of the pore volume in pores having diameters less than 7 nm which process comprises:

- (a) precipitating an aqueous solution of one or more aluminium salts by adjusting the pH of said solution to a range between 5.5 and 10.0 at a temperature in the range between 20 °C and 90 °C, thereby forming a precipitate,
- (b) ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 8.0 to 12.0,
- (c) washing the precipitate,

(d) mixing the precipitate with a nickel compound and a heavy metal compound wherein the heavy metal is selected from the group consisting of molybdenum, tungsten, and mixtures thereof, at a pH in the range between 4.0 and 10.0 at a temperature in the range between 25°C and 100°C until adsorption of the nickel and heavy metal compound onto the precipitate is sufficient to yield a final catalyst having from 1%w to 6%w nickel and from 8%w to 40%w heavy metal,

(e) extruding the product of step (d), and

(f) drying and calcining the product of step (e) at a temperature ranging from 300°C to 900°C.

It has been found that hydrogel-derived catalysts prepared according to the process according to the present invention have activities better than catalysts prepared by conventional techniques when compared on a volumetric basis. One of the major advantages of the hydrogel preparative technique is lower cost of catalyst manufacture relative to conventionally prepared impregnated catalysts even when the hydrogel derived catalysts have higher densities. The catalysts prepared according to the process according to the present invention have high surface areas, at least 300 m<sup>2</sup>/g, and at least 70% of the pore volume located in pores having diameters less than 7 nm. These catalysts are particularly suitable for tail end hydrocracking and hydrotreating applications in which high desulphurization activities and high hydrogenation abilities are desired.

The present invention also relates to catalysts prepared in accordance with the present invention and to the use of such catalysts in hydrotreating, in particular hydrodesulphurization of hydrocarbon feedstocks.

In the process according to the present invention, highly active catalysts are suitably prepared by

incorporating nickel and a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, into an alumina hydrogel prepared by titrating an aqueous solution of one or more aluminium salt(s) with a titrating agent.

The alumina hydrogel can be prepared by titrating an aqueous solution of one or more aluminium salt(s) with an appropriate acidic or basic material or solution as titrating agent to cause precipitation of the alumina gel. One skilled in the art will recognize that the alumina gel can be prepared by titrating an acidic aluminium salt such as, for example, aluminium sulphate, aluminium nitrate or aluminium chloride, in aqueous solution with a basic precipitating medium such as, for example, sodium hydroxide or ammonium hydroxide, or, by titrating an alkali metal aluminate such as, for example, sodium aluminate or potassium aluminate, in aqueous solution with an acidic precipitating medium such as, for example, hydrochloric acid or nitric acid. One skilled in the art will recognize that the adjustment of the pH of an aluminium-containing solution to between 5.5 and 10.0 will result in precipitation of the aluminium moiety as aluminium hydroxide or hydrated aluminium oxide.

In a preferred embodiment, the alumina hydrogel is prepared by titrating an aqueous solution of an alkali metal aluminate and an aqueous solution of an acidic-aluminium salt to cause precipitation of the alumina gel. Suitable acidic aluminium salts include aluminium sulphate, aluminium nitrate and aluminium chloride. A preferred species is aluminium sulphate. Suitable alkali metal aluminates are sodium aluminate and potassium aluminate. The precipitation can be carried out by adding an aqueous solution of the basic aluminium species to an aqueous solution of the acidic

aluminium species or the procedure can be reversed by adding an aqueous solution of the acidic aluminium species to an aqueous solution of the basic aluminium species (referred to as "sequential precipitation").

5 Preferably, the precipitation in the process according to the present invention is carried out by simultaneously adding the acidic aluminium species and the basic aluminium species to cause precipitation of the hydrogel (referred to as "simultaneous precipita-  
10 tion"). The maximum rate of addition of the acidic aluminium species and the basic aluminium species is fixed by the rate at which the two streams can be mixed and the effective control of the pH and the temperature of the system .

15 ~~The ranges and limitations provided in the present specification and claims are those which are believed to particularly point out and distinctly claim the present invention. It is, however, understood that other ranges and limitations that perform substantially~~  
20 ~~the same function in substantially the same manner to obtain the same or substantially the same result are intended to be within the scope of the present invention as defined by the present specification and claims.~~

25 The temperature and pH of the precipitation are important variables in the preparation of the aluminas into which metals can be incorporated to form catalysts with desirable physical qualities. One skilled in the art would recognize that changes in precipitation  
30 temperatures and pHs result in changes in porosities. The optimal temperatures and pHs for the precipitation of the aluminas can be determined with a minimal amount of routine experimentation. In the process according to the present invention, a precipitation temperature  
35 typically ranges from 20°C to 90°C, preferably from



50°C to 85°C, more preferably from 55°C to 65°C, and a precipitation pH typically ranges between 5.5 and 10.0, preferably between 5.5 and 8.0, and more preferably between 6.0 and 7.5. The length of time required for the precipitation step is typically from 15 minutes to 45 minutes. The period of time for the precipitation should be sufficiently long to allow adequate mixing of the materials, but not long enough for enhanced particle growth to occur.

After precipitation has taken place the pH of the slurry is adjusted to a pH in the range from 8.0 to 12.0, preferably 10.0 to 12.0, more preferably 11.0 to 12.0, and the resulting mass is aged at a temperature in the range from 20°C to 90°C, preferably 50°C to 85°C for at least 15 minutes. An upper limit on the length of time for ageing is not critical and is normally determined by economical considerations. Ageing times will typically range from 0.1 to 10 hours, preferably from 0.25 to 5 hours, and more preferably from 0.25 to 1 hour. In general, aluminas with acceptable properties are produced by holding the ageing temperature substantially equal to the precipitation temperature.

After ageing, the slurry is washed and filtered in routine fashion to remove substantially all of the removable water-soluble salts formed during the precipitation of the hydrogel. The preferred solvent for washing is water although other solvents such as lower alkanols may be utilized.

After washing, the metal compounds are incorporated into the hydrogel. One method for adding the metal compounds to the hydrogel is a reslurry step in which the hydrogel is reslurried with a solution containing solubilized salts of nickel and a heavy metal selected from the group consisting of molybdenum,

tungsten and mixtures thereof, sufficient to deposit on the final catalyst from 1%w to 6%w nickel and from 8%w to 22%w molybdenum or 10%w to 40%w tungsten. When mixtures of molybdenum and tungsten are utilized, the  
5 final catalyst contains from 8%w to 40%w molybdenum and tungsten. The solution may, however, contain amounts of nickel and molybdenum or tungsten in excess of that required to deposit the aforesaid amounts of metals, which excess may be removed by washing or other  
10 techniques following the reslurry step. A typical metal compounds containing solution can be prepared by combining a molybdenum and/or tungsten containing solution with a nickel containing solution.

The molybdenum solution comprises a water-soluble  
15 source of molybdenum oxide such as ammonium heptamolybdate or ammonium dimolybdate dissolved in water. Hydrogen peroxide may also be used to aid in solution preparation in some cases. A preferred method for preparing a molybdenum containing solution  
20 comprising adding hydrogen peroxide to the solution in an amount ranging from 0.1 to 1.0 mole of hydrogen peroxide per mole of molybdenum. Optionally, a suitable soluble amine compound such as monoethanolamine, propanolamine or ethylenediamine can  
25 be added to the molybdenum containing solution in order to aid in stabilization of the solution.

The tungsten containing solution typically comprises ammonium metatungstate dissolved in water. A preferred method for preparing a tungsten containing  
30 solution comprises adding hydrogen peroxide to the solution in an amount ranging from 0.1 to 1.0 mole of hydrogen peroxide per mole of tungsten. In addition, a suitable soluble amine compound such as monoethanolamine, propanolamine or ethylenediamine can

optionally be added to the tungsten containing solution in order to aid in stabilization of the solution.

The nickel containing solution comprises nickel compounds dissolved in water. A wide range of nickel compounds are suitable, such as nickel nitrate, nickel acetate, nickel formate, nickel sulphate, nickel oxide, nickel phosphate, nickel carbonate, nickel chloride, and nickel hydroxide. Two compounds that are especially useful are nickel nitrate and nickel carbonate.

An alternative method for incorporating the metal compounds into the hydrogel comprises adding dry, water-soluble metal compounds of nickel and dry, water-soluble compounds of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, to the hydrogel and mix until dissolution and adsorption of the metal compounds onto the gel is substantially complete. The metal compounds of nickel and molybdenum and/or tungsten are added to the hydrogel in amounts sufficient to incorporate into the final catalyst from 1%w to 6%w nickel and from 8%w to 22%w molybdenum or 10%w to 40%w tungsten. When mixtures of molybdenum and tungsten are utilized, the final catalyst contains 8%w to 40%w molybdenum and tungsten.

Molybdenum is generally added to the hydrogel as a dry, water-soluble source of molybdenum such as ammonium heptamolybdate or ammonium dimolybdate. Tungsten is typically added to the hydrogel as ammonium metatungstate. Nickel is preferably added to the hydrogel in the form of dry, water-soluble nickel nitrate, nickel acetate, nickel formate, nickel sulphate, nickel oxide, nickel phosphate, nickel carbonate, nickel chloride or nickel hydroxide, with nickel nitrate and nickel carbonate being preferred.

A preferred method of mixing the dry metal compounds of nickel and molybdenum and/or tungsten with the hydrogel comprises adding hydrogen peroxide to the mixture of dry metal compounds and hydrogel in an amount ranging from 0.1 to 1.0 mole of hydrogen peroxide per mole of molybdenum and/or tungsten. Optionally, a suitable amine compound such as monoethanolamine, propanolamine or ethylenediamine may be added to the mixture of dry metal compounds and hydrogel in order to aid in stabilization of the mixture of the metal compounds and the hydrogel.

The dry metal compounds of nickel and molybdenum and/or tungsten are typically added to the hydrogel in the form of finely divided particles which are generally 0.15 mm or less in size. While particle size is not critical and larger particle sizes may be utilized, it is economically advantageous to use particles which are 0.15 mm or less in size.

It is also within the scope of this invention to combine the two methods described above for adding the metals to the hydrogel. For example, one metal may be added to the hydrogel as a dry compound and another added in the form of a solution. Various permutations of this combination of dry compound additions and metals solutions additions would be obvious to one skilled in the art.

The temperature and pH of the step in which the metal containing solutions and/or the dry metal compounds are mixed with the hydrogel are important variables in the preparation of hydrogel-derived catalysts which have acceptable densities and porosities. The mixing of the hydrogel with the metal containing solution or the dry metal compounds is suitably carried out at a pH in the range between 4.0 and 10.0, preferably between 4.0 and 9.0, more

preferably between 5.0 and 8.0, and at a temperature in the range between 25°C and 100°C, preferably between 25°C and 80°C, until incorporation of the metals compounds into the <sup>precipitate</sup> ~~gel~~ is sufficient to yield a final calcined catalyst having from 1%w to 6%w nickel and from 8%w to 40%w heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof. Typically, the times for mixing the hydrogel and the metal compounds will range from 0.5 to 2 hours. Optionally, the resulting material can be washed to remove unadsorbed metals and filtered in routine fashion.

Following the addition of the metal compounds to the hydrogel, the material may be extruded and then dried and calcined; dried, milled with addition of water, extruded or pelleted and calcined; or partially dried, extruded or pelleted, dried more completely and calcined. Drying can be accomplished by conventional means. It may be carried out by forced draft drying, vacuum drying, air drying or similar means. Drying temperatures are not critical and depend upon the particular means utilized for drying. Drying temperatures will typically range from 50°C to 150°C.

In a preferred embodiment, the material is extruded and then dried. Alternatively, the material may be extruded after drying to the proper loss on ignition (LOI). In order to facilitate extrusion, organic binders and/or lubricants may be added prior to extrusion.

After drying, the material is calcined to produce the finished catalyst. The material may be calcined in a reducing, oxidizing or neutral atmosphere, although air is preferred. However, if binders and/or lubricants are used the material is suitably heated in an oxygen-containing atmosphere, preferably air, in



order to burn out the binders and lubricants.

Calcining temperatures will typically range from 300°C to 900°C. Drying, calcining and burn-out may be combined in one or two steps. Most frequently the calcining and/or burn-out steps are combined using an oxygen-containing atmosphere.

Certain other processing steps may be incorporated into the above-described procedure without deviating from the scope and intent of the process according to the present invention. For example, prior to the complete drying of the catalyst, it may be extruded and then dried more completely, followed by calcination.

The final catalysts are found to have surface areas greater than 300 m<sup>2</sup>/g, pore volumes ranging from 0.2 to 1.2 ml/g and with at least 70% of its pore volume in pores having diameters less than 7 nm, preferably less than 5 nm. In general, the metals contents of the final catalysts range from 1%w to 6%w, preferably from 3%w to 5%w nickel and from 8%w to 22%w, preferably about 14%w to 20%w molybdenum or 10%w to 40%w, preferably 18%w to 32%w tungsten.

The catalysts prepared in accordance with the process according to the present invention can be suitably applied to hydrocarbon conversion processes such as hydrocracking, hydrotreating, hydrogenation, dehydrogenation, alkylation, dealkylation and the like.

The catalysts prepared in accordance with the present invention are most commonly employed in hydrotreating and/or hydrocracking feedstocks ranging in volatilities from naphthas to petroleum residues, including materials derived from tar sands, shale oils and the like. Reaction temperatures will typically range from 150°C to 480°C, preferably from 260°C to 455°C. Reaction pressures are generally within the range from 14 to 240 bar, preferably from 40-175 bar.

Reactions are conducted at liquid hourly space velocities within the range of 0.05 to 15 reciprocal hour.

Multiple uses of these feedstocks after treating with the catalysts prepared in accordance with the present invention are possible. Depending on the particular feedstocks treated, suitable uses can include conversion unit feedstocks such as thermal cracking and hydrocracking, or finished products such as gasoline, diesel, airline turbine fuel, furnace oils, solvents, fuel oils and asphalts.

The process for preparing the catalysts in accordance with the present invention will be further described below by the following Examples which are provided for illustration and which are not to be construed as limiting the invention.

Example 1

Seven hundred and forty grams of reagent grade sodium aluminate were added to 1000 grams of water which was then heated to 60°C in order to effect dissolution of the materials. Seven hundred and thirty grams of  $\text{Al}_2(\text{SO}_4)_3 \cdot 17 \text{H}_2\text{O}$  were added to 760 grams of water. Both solutions were cooled to slightly less than 60°C and placed in dropping funnels.

Five thousand grams of water were added to a 10 litre stainless steel bucket equipped with a pH meter, thermometer and stirrer, to serve as the heel. The two solutions in the dropping funnels were added simultaneously to the well-stirred bucket until the aluminium sulphate solution was exhausted, maintaining a precipitation pH of 7.0. The remainder of the sodium aluminate solution was added to raise the final ageing pH of the solution to between 11.0 and 12.0. The solution was aged for one hour at 60°C. The resulting material was filtered and washed in two large Buchner

funnels with about 50 litres of water. The excess water from the wet filter cake was removed by vacuum. The hydrogel was then divided into two equal portions.

5 The following solutions were then prepared. 45.9 Grams of nickel nitrate as hexahydrate was diluted to 750 millilitres with water. An additional solution of 68.1 grams of ammonium heptamolybdate and 10.5 ml of 30% hydrogen peroxide were diluted to 750 millilitres with water. The two solutions were added and  
10 reslurried with one-half of the hydrogel at 80°C for two hours at pH of 5.5. At the end of two hours, the slurry was filtered and washed with three litres of water. The excess water from the slurry was removed by vacuum. The wet gel was then extruded using a small,  
15 hand-held extruder using a 0.4 mm cylindrical die, dried overnight at 120°C and calcined in air at 510°C. The properties of the catalyst are listed in Tables I and II.

#### Comparative Example A

20 A catalyst was prepared using a conventional dry pore volume impregnation technique. A solution suitable for impregnating 100 grams of a gamma alumina carrier was prepared as follows. A solution was prepared by adding 30.28 grams of ammonium dimolybdate to 62  
25 millilitres of 24% ammonia. The solution was then heated to 40°C and stirred in order to effect dissolution of the materials. 7.64 Grams of nickel carbonate was then added to the solution. When the solution became clear, the solution was added to the  
30 gamma alumina support in several small portions with intermediate agitations. The impregnated support was further agitated for a period of about 5 minutes, dried for 2 hours at 120°C and calcined in air for 2 hours at 482°C. The properties of the catalyst are listed in  
35 Tables I and II.

### Catalyst Testing

Catalyst samples were used to hydrotreat a catalytically-cracked heavy gas oil (CCHGO) in a trickle-flow reactor. Ten ml of the appropriate extruded catalyst were crushed and sieved to 0.3-1 mm (16-45 mesh), diluted with silicon carbide, and loaded into a typical trickle-flow reactor tube. The catalyst was presulphided with a 5%  $H_2S/H_2$  (v/v) gas mixture at  $371^\circ C$  for 2 hours prior to testing. A CCHGO was passed over the catalyst at  $375^\circ C$  and a hydrogen partial pressure of 58.6 bar with a  $H_2$ /oil ratio equal to 4.0. Measured rate constants include hydrogenation, denitrification and desulphurization and are reported relative to the non-hydrogel catalyst (Comparative Example A) and are calculated on a volumetric basis. Specific catalyst performance characteristics are presented in Table III.

TABLE I

### Catalyst Properties

|                                                             |           |      |
|-------------------------------------------------------------|-----------|------|
| Ageing pH <sup>a)</sup>                                     | 11.0-12.0 | --   |
| Density g/ml <sup>b)</sup>                                  | 1.10      | 0.76 |
| Reslurry pH <sup>c)</sup>                                   | 5.5       | --   |
| N <sub>2</sub> Surface Area m <sup>2</sup> /g <sup>d)</sup> | 399       | 216  |
| N <sub>2</sub> Pore Volume ml/g <sup>e)</sup>               | 0.32      | --   |
| %wt. Nickel <sup>f)</sup>                                   | 4.6       | 3.2  |
| %wt. Molybdenum <sup>g)</sup>                               | 19.2      | 13.3 |

TABLE II

Catalyst Pore Size Distributions

|    | Hg Pore <sup>h)</sup><br>Size Dist                                                                                                                                                                | COMPARATIVE |           |
|----|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|-----------|
|    |                                                                                                                                                                                                   | EXAMPLE 1   | EXAMPLE 1 |
|    | < 5 nm                                                                                                                                                                                            | 88.9        | 2.4       |
|    | 5 - 7 nm                                                                                                                                                                                          | 4.7         | 6.3       |
|    | 7 - 10 nm                                                                                                                                                                                         | 3.0         | 36.7      |
|    | 10 - 15 nm                                                                                                                                                                                        | 1.8         | 42.7      |
|    | 15 - 35 nm                                                                                                                                                                                        | 1.6         | 7.9       |
|    | > 35 nm                                                                                                                                                                                           | 0.0         | 4.0       |
|    | a) Measured using an Orion 231 pH meter and Orion electrodes.                                                                                                                                     |             |           |
|    | b) 209 ml volume fully settled in a graduated cup and weighed.                                                                                                                                    |             |           |
| 5  | c) Measured using an Orion 231 pH meter and Orion electrodes.                                                                                                                                     |             |           |
|    | d) BET (Brunauer, S., Emmet, P. Y. and Teller, E. J. Am. Chem. Soc., 60, 309-316 (1938)) by nitrogen adsorption/desorption, Micromeritics Digisorb 2500 Instrument.                               |             |           |
| 10 | e) By nitrogen adsorption, Micromeritics Digisorb 2500 Instrument.                                                                                                                                |             |           |
|    | f) Weight percent determined by neutron activation analysis or atomic absorption spectroscopy.                                                                                                    |             |           |
| 15 | g) Weight percent determined by neutron activation analysis or atomic absorption spectroscopy.                                                                                                    |             |           |
|    | h) Determined by mercury intrusion, to 4136 bar using a Micromeritics Autopore 9210, using a 130° contact angle and 0.473 N/m surface tension of mercury. Numbers listed are percent pore volume. |             |           |
| 20 |                                                                                                                                                                                                   |             |           |

TABLE III  
Specific Catalyst Performance

|                       | <u>CCHGO (VOLUMETRIC BASIS)</u> |          |          |
|-----------------------|---------------------------------|----------|----------|
|                       | <u>H</u>                        | <u>N</u> | <u>S</u> |
| Example 1             | 1.12                            | 1.39     | 1.42     |
| Comparative Example A | 1.00                            | 1.00     | 1.00     |

H = Hydrogenation

N = Denitrogenation

S = Desulphurization

The claims defining the invention are as follows:

1. A process for preparing highly active catalysts having surface areas of at least  $300 \text{ m}^2/\text{g}$  and at least 70% of the pore volume in pores having diameters less than 7 nm, which process comprises:
  - (a) precipitating an aqueous solution of one or more aluminium salt(s) by adjusting the pH of said solution to a range between 5.5 and 10.0 at a temperature in the range between  $20^\circ\text{C}$  and  $90^\circ\text{C}$ , thereby forming a precipitate,
  - (b) aging the precipitate at a temperature ranging from  $20^\circ\text{C}$  to  $90^\circ\text{C}$  for at least 15 minutes at a pH ranging from 8.0 to 12.0,
  - (c) washing the precipitate,
  - (d) mixing the precipitate with a nickel compound and a heavy metal compound wherein the heavy metal is selected from the group consisting of molybdenum, tungsten, and mixtures thereof, at a pH in the range between 4.0 and 10.0 at a temperature in the range between  $25^\circ\text{C}$  and  $100^\circ\text{C}$  until adsorption of the nickel and heavy metal compound onto the precipitate is sufficient to yield a final catalyst having from 1%w to 6%w nickel and from 8%w to 40%w heavy metal,
  - (e) extruding the product of step (d), and
  - (f) drying and calcining the product of step (e) at a temperature ranging from  $300^\circ\text{C}$  to  $900^\circ\text{C}$ .
2. A process according to claim 1, wherein step (a) comprises titrating the aqueous solution of one or more aluminium salt(s) with a titrating agent, thereby forming the precipitate.
3. A process according to claim 1, wherein step (d) comprises mixing the precipitate with one or more solution(s) containing solubilized salts of nickel and heavy metal.
4. A process according to claim 1, wherein step (d) comprises mixing the precipitate with dry, water-soluble salts of nickel and dry, water-soluble salts of heavy metal.
5. A process according to claim 2, wherein step (a) comprises titrating an aqueous solution of an acidic aluminium salt with an aqueous solution of a basic aluminium compound and wherein step (d) comprises mixing the precipitate with one or more solution(s) containing solubilized salts of nickel and heavy metal.
6. A process according to claim 5, wherein step (d) comprises mixing the precipitate with dry, water-soluble salts of nickel and dry, water-soluble salts of heavy metal.

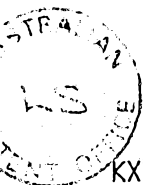
7. A process according to claim 2, wherein step (a) comprises titrating an aqueous solution of an acidic aluminium salt selected from the group consisting of aluminium sulphate, aluminium nitrate and aluminium chloride, with an aqueous solution of a basic aluminium compound selected from the group consisting of sodium aluminate and potassium aluminate and wherein step (d) comprises mixing the precipitate with one or more solution(s) containing solubilized molybdate or dimolybdate salts and nickel salts<sup>at a pH</sup> in the range between 4.0 and 9.0 until absorption of nickel and molybdenum onto the precipitate is sufficient to yield a final catalyst having from 3%w to 5%w nickel and from 14 to 20% molybdenum.

8. A process according to claim 7, wherein step (d) comprises mixing the precipitate with dry, water-soluble nickel salts and dry, water-soluble molybdate or dimolybdate salts.

9. A process according to claim 2, wherein step (a) comprises titrating an aqueous solution of an acidic aluminium salt selected from the group consisting of aluminium sulphate, aluminium nitrate and aluminium chloride, with an aqueous solution of a base at a pH in the range between 5.5 and 8.0 and wherein step (d) comprises mixing the precipitate with one or more solution(s) containing solubilized molybdate or dimolybdate salts and nickel salts at a pH in the range between 4.0 and 9.0 until adsorption of nickel and molybdenum onto the precipitate is sufficient to yield a final catalyst having from 3%w to 5%w nickel and from 14%w to 20%w molybdenum.

10. A process according to claim 9, wherein step (d) comprises mixing the precipitate with dry, water-soluble nickel salts and dry, water-soluble molybdate or dimolybdate salts.

11. A process according to claim 2, wherein the step (a) comprises titrating an aqueous solution of an acid with an aqueous solution of a basic aluminium compound selected from the group consisting of sodium aluminate and potassium aluminate at a pH in the range between 5.5 and 8.0 and wherein step (d) comprises mixing the precipitate with one or more solution(s) containing solubilized molybdate or dimolybdate salts and nickel salts at a pH in the range between 4.0 and 9.0 until adsorption of nickel and molybdenum onto the precipitate is sufficient to yield a final catalyst having from 3%w to 5%w nickel and from 14%w to 20%w molybdenum.



12. A process according to claim 11, wherein step (d) comprises mixing the precipitate with dry, water-soluble nickel salts and dry, water-soluble molybdate or dimolybdate salts.

13. A process according to any one of claims 1 to 12, wherein step (b) is carried out at a pH in the range between 10.0 and 12.0.

14. A process according to any one of claims 1-6, wherein step (d) is carried out at a pH in the range between 4.0 and 9.0.

15. A process according to any one of claims 1-6 wherein a final catalyst is obtained containing from 3%w to 5%w nickel and from 8%w to 22%w molybdenum.

16. A catalyst which comprises a catalytically effective amount of nickel and a catalytically effective amount of a heavy metal selected from the group consisting of molybdenum, tungsten or mixtures thereof on a support said catalyst having a surface area of at least  $300 \text{ m}^2/\text{g}$  and at least 70%w of the pore volume in pores having diameters less than 7 nm and wherein said catalyst has been prepared by a process according to any one of claims 1 to 15.

17. A process for desulphurizing hydrocarbon feedstocks wherein a catalyst is used which has been prepared by a process according to any one of claims 1 to 15.

18. A process for preparing highly active catalysts having surface areas of at least  $300 \text{ m}^2/\text{g}$  and at least 70% of the pore volume in pores having diameters less than 7 nm, substantially as hereinbefore described with reference to the Example.

19. A catalyst which comprises a catalytically effective amount of nickel and a catalytically effective amount of a heavy metal selected from the group consisting of molybdenum, tungsten or mixtures thereof on a support said catalyst having a surface area of at least  $300 \text{ m}^2/\text{g}$  and at least 70%w of the pore volume in pores having diameters less than 7 nm and wherein said catalyst has been prepared by a process according to claim 18.

20. A process for desulphurizing hydrocarbon feedstocks wherein a catalyst is used which has been prepared by a process according to claim 18.

DATED this SEVENTEENTH day of OCTOBER 1990  
Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant  
SPRUSON & FERGUSON



KXW:1043y