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PATENT SPECIFICATION (11) 1 518 878

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(21) Application No. 16353/76 (22) Filed 22 April 1976
(31) Convention Application No. 577328
(32) Filed 14 May 1975 in
(33) United States of America (US)
(44) Complete Specification published 26 July 1978
(51) INT CL² B01J 23/74
(52) Index at acceptance
B1E 262 285 291 293 308 330 33Y 422 42Y 541 551 55Y 562 578 645 650 693 780 78X 78Y



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(54) ACTIVATED MASSIVE NICKEL CATALYST AND ITS PREPARATION

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the activation of nickel-silica catalysts which contain very little quantities of alkaline metals. In one aspect, this invention relates to the addition of copper in the preparation of a massive nickel hydrogenation catalyst thereby facilitating the low temperature reduction of the catalyst.

The so-called activation of supported nickel catalysts, i.e., the reduction of nickel oxide before the catalyst is utilized, is usually conducted at temperatures which are very high in comparison to those at which the reduction of bulk nickel oxide can be completed. It is a well-known fact that supported nickel oxide is more difficult to reduce than when unsupported and that high reduction temperatures promote sintering of nickel. It is thought that, in many instances, a better activity and/or a better poison capacity could be obtained, if lower reduction temperatures could be used.

In conformity with the experience of people concerned with catalyst manufacture, recent publications suggest that various promoters of nickel catalyst are effective not because of some modification of the catalytic properties, but as a consequence of a better activitation.

A. Roman and B. Delmon in an article from the *Journal of Catalysis, 30,* pp. 333—342 (1973) entitled "Promoter and Carrier Effects in Reduction of NiO/SiO_2" have described the hydrogen reduction of nickel oxide deposited on silica by employing copper deposited onto the surface of the catalyst.

In another paper published in the *Journal of Catalysis, 22,* pp. 204—212 (1971) entitled "Increase of Reductibility of NiO by H_2, Due to Pretreatment with Salt Solutions" by H. Charcosset, R. Frety, A. Soldat and Y. Trambouze, is described the use of copper in the treatment of pure nickel oxide to make the reduction easier. As described in this paper, they also impregnated the nickel oxide catalyst with various salt solutions followed by drying and extraction with water. They then compared the reduction of these catalysts in hydrogen to see which metals had the most effect. They indicated most pronounced effects occur with copper, platinum, palladium, ruthenium, rhodium, osmium and iridium which they stated are related to a cationic exchange with surface nickel during impregnation.

More recently, in a paper published in the *Journal of Catalysis, 24,* pp. 283—296 (1972) entitled "Catalytic Hydrogenolysis and Dehydrogenation Over Copper-Nickel Alloys" by J. H. Sinfelt, J. L. Carter and D. J. C. Yates, there is described the surprisingly large effects on suppression of hydrocracking from the incorporation of small amounts of copper into nickel in a copper/nickel alloy.

The patent literature also includes descriptions of nickel catalysts which contain copper. One example of such a description is disclosed in U.S. Patent No. 2,750,261 to Ipatieff et al. In this patent there is disclosed a process for preparing catalyst useful in the production of hydrogen comprising the steps of co-precipitating a mixture of nickel and copper ions onto a carrier such as diatomaceous earth.

The copper promotion of the invention relates to the massive nickel catalyst described in U.S. Patent Nos. 3,697,445 and 3,859,370. These patents describe catalysts

having high nickel surface area and the relationship between the high nickel surface area and their activity. The nickel surface area is measured in the manner described by Yates, Taylor and Sinfelt in *J. Am. Chem. Soc. 86*, 2996 (1964).

In U.S. Patent 3,859,370 there is described a process for carefully controlling critical conditions to form these high nickel surface area catalysts wherein nickel catalysts precipitated in the presence of porous solid particles can be made which have a nickel surface area greater than about 70 m^2/g, preferably 75 to 100 m^2/g and catalytic activity for hydrogenation several times greater than the previously known nickel catalysts.

The massive nickel catalysts described in the aforesaid patents have proven to be active hydrogenation catalysts in laboratory and pilot plant runs when they are activated by reduction at 400°C. However, there is a need to have such a catalyst that can be activated at the lower temperatures that are normally obtainable in the commercial hydrogenation plant which are of the order of approximately 200°C.

It has been discovered that the presence of copper ions during the coprecipitation of the nickel and silica ions provides a catalyst which can be activated at lower temperatures than are normally required for nickel-containing hydrogenation catalysts. Specifically, it has been found that by the incorporation of copper in a massive nickel catalyst during the co-precipitation provides a highly active hydrogenation catalyst which can be activated at temperatures of approximately 200°C.

Accordingly to this invention consists in a copper-nickel-silica catalyst having a B.E.T. total surface area ranging from 150 to 300 m^2/g, wherein the amount of copper in the catalyst ranges from 2 wt. % to 10 wt. % and the amount of nickel ranges from 25 wt. % to 50 wt. % said wt. % of copper and nickel being based on the total weight of the catalyst.

B.E.T. standing for Brunauer-Emmett-Teller is a standard test for determining total surface area of materials such as catalysts (see The Van Nostrand Chemist's Dictionary).

In one embodiment of the present invention there is provided a copper promoted massive nickel catalyst which is capable of having a reduced nickel surface area ranging from 55 to 100 m^2/g as determined by hydrogen chemisorption after reduction, at 400°C.

In another embodiment of the present invention there is provided a process for hydrogenating organic compounds by contacting a hydrogenatable organic compound with hydrogen in the presence of a reduced copper promoted massive nickel-silica catalyst capable of having a reduced metal surface area ranging from 55 to 100 m^2/g as determined by hydrogen chemisorption, after reduction at 400°C., and a B.E.T. total surface area ranging from 150 to 300 m^2/g.

Unlike the prior art publications that show the addition of copper to the surface of the nickel oxide, the copper must be added to these massive nickel systems during the precipitation stage through the use of separate solutions which are preferably aqueous in nature. In a first solution, there is dissolved a source of silicate anion and in a second solution, a source of nickel cation and copper cation. Slurried within the solution containing the silicate anion is a porous support, preferably a porous silica support such as kieselguhr. The two solutions are comingled by addition of the nickel-copper containing solution to the silicate solution over a period usually of 5 to 40 minutes. By comingling the two previously prepared solutions, the amount of dissolved nickel in the reaction mixture is kept exceedingly low and below 0.60 moles/liter of aqueous mixture. This dilution of the dissolved nickel ions is essential in obtaining high nickel surface area catalysts. Also, the addition should preferably be made at a substantially constant rate accompanied by vigorous mixing to increase uniformity in the catalyst formation. The mixture is then heated preferably to its boiling point, and a precipitating agent is added. A commonly used precipitating agent is ammonium bicarbonate.

During the preparation it is preferred that water is added to maintain a nearly constant volume so that water lost by evaporation is continually replaced. The aqueous mixture is kept at its boiling point for a period of 1 to 5 hours; it is then filtered and the resulting product is washed repeatedly with boiling water. Next the catalyst is dried and calcined in oxygen source. The finished catalyst can then be charged directly into the reaction vessel, without activation, and activated in the reaction vessel with a gaseous reductant, usually flowing hydrogen.

As stated previously, the copper-nickel containing solution and the silicate-containing solution are comingled under conditions of dilution such that the amount of dissolved nickel ions in the resultant aqueous mixture is maintained exceedingly low thereby providing for a high nickel surface area catalyst. Additionally, however, it is preferred that in preparing the catalyst of this invention the precipitation of the catalyst be made from dilute solutions, i.e. in addition to the nickel-containing solution having a nickel concentration no greater than 0.6 moles/liter it is preferred that for the other solution the silicate ion concentration should be no greater than 0.35 moles/liter. The copper concentra-

tion is determined by the desired amount of copper in the catalyst. The most preferred solution used in preparing the catalyst has no more than 0.26 moles/liter of silicate ion. This is contrasted with a more concentrated precipitation in which the solution contains up to twice as much solute.

30 to 90 wt. percent of the total silica content of the activated catalyst derives from precipitated silicate ions. Preferably, however, 50 to 70 wt. percent of the total silica content is derived from silicate ions.

The remaining steps in preparing and activating the catalyst are identical to those described above.

In more detail, this invention pertains to the production of an improved catalyst for hydrogenation. The catalyst may be used to hydrogenate aromatics as typified by the hydrogenation of benzene to cyclohexane, the hydrogenation of aldehydes, both saturated and unsaturated to the alcohols as in the well-known oxo process, the hydrogenation of the double bonds in edible fats and oils as well as other olefins both straight and branched chain, the hydrogenation of aromatics in white oil base stocks to produce high grade white oils and the hydrogenation of nitro compounds to amines. Indeed, olefins as used herein signify unsaturated compounds having at least one multiple bond and contemplate polyunsaturated compounds as well.

To form the catalyst, nickel and copper, as well as the silicate ions must be coprecipitated onto a porous solid particulate support, preferably a porous silica particulate support. Initially, two distinct solutions are prepared; in one of these solutions is a silicate ion source such as alkali silicates, e.g. sodium and potassium silicates, sodium meta silicate, silicic acid or hydrolyzed silicon hydride.

A second solution, containing a source of nickel cation and copper cation is also prepared; the source of nickel cation may be any of the following: nickel nitrate, nickel chloride and nickel bromide. The source of copper cation may be also copper nitrate, copper chloride and copper bromide.

Other sources of nickel cation and silicate anion may be utilized and will be obvious to one skilled in the art.

Porous solid particles, preferably silica particles, are slurried in the silicate anion solution. In particular, kieselguhr, silica or alumina may be used as the source of the porous particles. The concentration of kieselguhr, as the porous solid particles can be from 10 to 70 percent, preferably from 30 to 50 percent by weight of the total silica in the catalyst.

The two solutions, one solution containing copper and nickel cations, the other containing the silicate anion are comingled at a slow rate to effect maximum mixing. Typically, the amount of nickel metal ranges from 5 to 60 gm/litre and the amount of copper ranges from 0.2 to 12 gm/litre, and the nickel and copper nitrate solution can be added to a sodium metasilicate solution uniformly over a 5 to 40 minutes period, preferably 10 to 30 minute period. The mixture is then heated, preferably to the boiling point and coprecipitation of copper nickel and silicate ions must be completed. This may be effected by various methods known in the art, but it is most preferred that the coprecipitation of copper, nickel and silicate ions in aqueous solution containing the solid carrier particles be completed by addition of a water soluble alkaline precipitating compound such as ammonium bicarbonate. The alkaline ammonium precipitants are most suitable for minimizing the amount of alkali metal residue which has to be removed by washing to avoid poisoning action on the finished catalyst. In some instances, the potassium precipitants may be used where the potassium acts as a promoter rather than as a poison.

The salts of the metal are preferably the water-soluble compounds, e.g. nitrates, chlorides, formates or oxalates.

Following the precipitation, the mixture is preferably maintained at the boiling point for 1 to 5 hours; then it is filtered and washed 4 times with boiling water. Precipitated catalyst is then dried by heating for 1 to 5 hours at a temperature of 90 to 200°C. It is then calcined by heating in the presence of an oxygen-containing gas or air to a temperature in the range of 300 to 450°C. for a period of 2 to 8 hours, preferably 3 to 5 hours.

After the calcining is completed, the catalyst must be reduced in order to acitvate it. Reduction is carried out in the presence of a reducing gas which is preferably hydrogen. Hydrogen is passed over the catalyst at ambient temperature at a rate of 5 1/hr/gm catalyst to 100 1/hr/gm catalyst, preferably 10 1/hr/gm to 30 1/hr/gm and then the temperature is raised to a range from 75°C. to 400°C., preferably 80°C to 250°C.

The reduction is preferably carried out after the catalyst has been loaded into the reaction vessel, where the hydrogenation will be carried out, which may be either batch or continuous, the nature of the reactor will be obvious to one skilled in the art.

The resulting catalyst has a total surface area of 150 to 300 m^2/g and usualy a nickel surface area of 55 to 100 m^2/g. Also, the catalyst contains from 25 wt. % to 50 wt. % of nickel and usually 0.1 wt. % or less of sodium.

One particularly useful hydrogenation is the conversion of benzene to cyclohexane.

Another useful hydrogenation is the conversion of aromatics in white spirits to yield

high quality solvents. The upgrading of white spirits by the process of this invention is an improvement in the treatment of such materials.

Another useful improved hydrogenation is the conversion of olefins in paraffin solvents such as denonenizer bottoms and deoctenizer overheads.

The conditions for the hydrogenation reactions which have been discussed vary widely and are well known to those skilled in the art; broadly the following conditions may be utilized: temperatures 75—450°C.; pressure 1 atm.—12,000 psig; feed rate 0.2—100 v/hr/v; H_2 rate of 2,000—10,000 SCF/B.

The oxo process is the addition of carbon monoxide and hydrogen to alkenes in order to produce alcohols, aldehydes and other oxygenated organic compounds. Typical alkenes which may be utilized in the process are those having 2 to 20 carbon atoms per molecule; conditions for the oxo process are temperatures of 70 to 175°C.; hydrogen to hydrocarbon mol ratio of 0.5 to 10.0 and a pressure of 100 to 1000 psig.

The product of such a carbonylation process generally consists of aldehydes, acetals, unsaturated oxygenated materials and the like which require hydrofinishing in a second or further hydrogenation stage. It is to the treatment of the aldehyde product, in particular, that the present invention applies.

Hydrogenation conditions in this further reaction stage follow those generally employed in the first stage.

EXAMPLE 1

Catalyst A was prepared as follows: 8.75 gm. of $Cu(NO_3)_2 \cdot 3H_2O$ and 112 gm. of $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 500 ml of distilled water, then 38 gm. of $Na_2SiO_3 \cdot 9H_2O$ was dissolved in another 500 ml of water and 5 gm. of acid washed kieselguhr was slurried in this second solution. The second solution with the kieselguhr slurried therein was stirred vigorously while the first solution containing the copper and nickel salts was added at a uniform rate over a 20 minute period. This mixture was then heated to the boiling point and 80 gm. of NH_4HCO_3 was added at a uniform rate over a 20 minute period. The mixture was kept at the boiling point for 3 hours while stirring continued. It was then filtered and washed 5 times with boiling water, each wash consisting of 500 ml of water. The filtercake was then dried at 120°C. and calcined in air for 4 hours at 400°C.

The reduced nickel surface area of Catalyst A was determined by hydrogen chemisorption, after reduction at 400°C., to be 62.0 m^2/g.

Catalyst B was prepared in the same manner as Catalyst A with the exception that there was no copper added.

Catalyst B had a reduced nickel surface area of 65 m^2/g as determined by hydrogen chemisorption after reduction at 400°C. and a B.E.T. total surface area of 292 m^2/g.

Table I demonstrates the data from thermogravemetric analysis experiments which are presented for two massive nickel catalysts; one with 5 wt.% copper (Catalyst A) added during the precipitation step and the other (Catalyst B) without any copper added. The Table shows that the copper-containing catalyst starts to reduce significantly at about 200°C. lower than the catalyst without copper. It also shows that Catalyst A is substantially reduced at temperatures that can be reached in commercial hydrogenation plants whereas Catalyst B does not start to reduce significantly below 350°C.

EXAMPLE 2

The data in Table II compares two catalysts for the hydrogenation of benzene. They are Catalyst A and a catalyst made by the same procedure as Catalyst A (Catalyst E) but there was no copper used in the preparation. The catalysts were pre-reduced and stabilized then re-reduced in the reactor at 204°C. This temperature is not adequate to activate the catalyst that does not contain copper and it can be seen that the conversion of benzene to cyclohexane is much greater over the copper-containing catalyst.

TABLE I

Temperature	Catalyst A Extent of Reduction Based on reductive and nonreductive thermogravemetric analysis	Catalyst B
100°C.	19%	14%
150°C.	22%	17%
200°C.	32%	18%
250°C.	50%	18%
300°C.	72%	19%
350°C.	100%	21%
400°C.	100%	33%
450°C.	100%	57%

TABLE II

	Catalyst A 5 wt.% copper	Catalyst E No copper
Conversion of benzene to cyclohexane after 1 hour on stream	30.5%	15%
Run Conditions:	Temp. 100°C. Press. 1 atm. S.V. 25 W/Hr/W H_2/C_6H_6 50 mol ratio	

EXAMPLE 3

Catalyst C, which was prepared in the same manner as Catalyst A of Example 2, was tested and compared with Catalyst B

in a manner designed to simulate conditions used in solvent hydrogenation. Catalyst C had a reduced nickel surface area of 65.4 m^2/g as determined by hydrogen chemisorption after reduction at 400°C. and a B.E.T. total surface area of 275 m^2/g. The feed was 15 wt. % benzene in cyclohexane and the pressure was 70 psig. The data in Table III shows that Catalyst C can be activated under conditions used in the plant and has high activity whereas the catalyst without copper (Catalyst B) shows almost no activity.

TABLE III

	Temp. °C.	S.V. W/Hr/S	wt. % C_6H_6	% Conversion of the C_6H_6
Catalyst C 5 wt. % Cu	200	18.8	0	100
Catalyst B No Cu	202	18.8	14.9	0.7

Run Conditions: Press. 70 psig, H_2 to Hydrocarbon 10.5 mol. ratio Feed, 15 wt. % benzene in cyclohexane

EXAMPLE 4

A further illustration of the low temperature activation of this catalyst is given in Table IV where we show the active nickel surface area for two catalysts, with and without copper, which were obtained after reduction at 200°C. Catalyst D was prepared in the same manner as Catalyst B of Example 1. (Catalyst C had a reduced nickel surface area of 65.4 m^2/g and Catalyst D had a reduced nickel surface of 64.3 m^2/g both as determined by hydrogen chemisorption after reduction at 400°C.)

TABLE IV

	Catalyst C wt. 5% Cu	Catalyst D No Copper
Active nickel surface area, $m^2/gm.$ catalyst	34.1	3.9

Therefore, the new copper-nickel-silica catalyst disclosed in this example can be charged into the hydrogenation plant without undergoing the customary pre-reduction and stabilization steps that are required for the commercial hydrogenation catalysts now being used. It is clearly shown that the catalyst containing the copper is easily reduced and develops a substantial active nickel surface area whereas the catalyst without copper does not reduce nor develop an active nickel surface area to any significant extent.

EXAMPLE 5

This experiment was run to show the importance of adding the copper during the precipitation of the catalyst. In Catalyst A (as prepared in Example 1), the copper was coprecipitated withe the nickel, according to the invention. Catalyst F was prepared by impregnating 6.85 g of the dried but uncalcined powder used to make Catalyst B with 4.8 ml of an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ of proper concentration to give 5 wt. % Cu on the reduced catalyst. The catalyst was then dried at 230°F. and calcined 4 hours at 750°F. The results are shown in Table V.

TABLE V

Temp., °C.	Catalyst A Percent Extent of Reduction Based on Total Loss in H_2 at 700°C.	Catalyst F
0	0	0
100	11	11
150	24	16
200	33	20
250	42	23
300	52	25
350	63	29
400	75	36
450	84	50

These results demonstrate the criticality in coprecipitating the Cu and Ni with the silicate anion as opposed to adding them to the surface of the NiO as taught in the prior art.

WHAT WE CLAIM IS:—

1. A copper-nickel-silica catalyst having a B.E.T. total surface area ranging from 150 to 300 m^2/g, wherein the amount of copper in the catalyst ranges from 2 wt. % to 10 wt. % and the amount of nickel ranges from 25 wt. % to 50 wt. %, said wt. % of copper and nickel being based on the total weight of the catalyst.

2. A catalyst in accordance with claim 1 wherein the catalyst contains 0.1 wt. % or less of sodium based on the total weight of the active catalyst and a reduced nickel surface area ranging from 55 to 100 m^2/g as determined by hydrogen chemisorption after reduction at 400°C.

3. A catalyst in accordance with either of claims 1 and 2 wherein the catalyst contains porous solid particles.

in a manner designed to simulate conditions used in solvent hydrogenation. Catalyst C had a reduced nickel surface area of 65.4 m^2/g as determined by hydrogen chemisorption after reduction at 400°C. and a B.E.T. total surface area of 275 m^2/g. The feed was 15 wt. % benzene in cyclohexane and the pressure was 70 psig. The data in Table III shows that Catalyst C can be activated under conditions used in the plant and has high activity whereas the catalyst without copper (Catalyst B) shows almost no activity.

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A further illustration of the low temperature activation of this catalyst is given in Table IV where we show the active nickel surface area for two catalysts, with and without copper, which were obtained after reduction at 200°C. Catalyst D was prepared in the same manner as Catalyst B of Example 1. (Catalyst C had a reduced nickel surface area of 65.4 m^2/g and Catalyst D had a reduced nickel surface of 64.3 m^2/g both as determined by hydrogen chemisorption after reduction at 400°C.)

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These results demonstrate the criticality in coprecipitating the Cu and Ni with the silicate anion as opposed to adding them to the surface of the NiO as taught in the prior art.

WHAT WE CLAIM IS:—

1. A copper-nickel-silica catalyst having a B.E.T. total surface area ranging from 150 to 300 m^2/g, wherein the amount of copper in the catalyst ranges from 2 wt. % to 10 wt. % and the amount of nickel ranges from 25 wt. % to 50 wt. %, said wt. % of copper and nickel being based on the total weight of the catalyst.

2. A catalyst in accordance with claim 1 wherein the catalyst contains 0.1 wt. % or less of sodium based on the total weight of the active catalyst and a reduced nickel surface area ranging from 55 to 100 m^2/g as determined by hydrogen chemisorption after reduction at 400°C.

3. A catalyst in accordance with either of claims 1 and 2 wherein the catalyst contains porous solid particles.

4. A catalyst in accordance with any one of the preceding claims wherein the porous solid particles are kieselguhr, silica or alumina.

5. A catalyst in accordance with either of claims 3 and 4 wherein the porous solid particles are kieselguhr and the concentration of the porous solid particles ranges from 10 wt. % to 70 wt. % of the total silica in the catalyst.

6. A catalyst in accordance with claim 5 wherein the concentration of the porous solid particles ranges from 30 wt. % to 50 wt. % based on the total silica in the catalyst.

7. A catalyst in accordance with any one of the preceding claims which has a nickel surface area of 55 to 100 m^2/g.

8. A catalyst in accordance with any one of the preceding claims wherein the catalyst has been reduced to an active state.

9. A process for making a copper-promoted--nickel-silica catalyst in accordance with claim 1 comprising:

(a) uniformly comingling an aqueous slurry containing silicate anions and solid porous particles with nickel and copper cations under conditions of dilution such that the amount of dissolved nickel in the comingled reaction solution is below 0.60 moles/litre;
(b) heating the comingled reaction mixture; and
(c) adding a precipitating agent to coprecipitate the copper nickel and silicate ions onto said solid porous carrier particles.

10. A process in accordance with claim 9 wherein the catalyst is capable of having a reduced nickel surface area ranging from 55 to 100 m^2/g as determined by hydrogen chemisorption after reduction at 400°C.

11. A process in accordance with either of claims 9 and 10 wherein the amount of copper in the catalyst ranges from 2 to 10 wt. % based on the total weight of the catalyst.

12. A process in accordance with any one of the claims 9 to 11 therein the precipitating agent is a water soluble alkaline precipitating agent.

13. A process in accordance with claim 12 wherein the precipitating agent is ammonium bicarbonate.

14. A process in accordance with any one of claims 9 to 12 wherein said catalyst is dried and calcined at a temperature of between 300 and 450°C.

15. A process in accordance with any one of claims 9 to 14 wherein said catalyst is reduced at a temperature of between 75°C. and 400°C.

16. A process in accordance with claim 15 wherein said catalyst is reduced at a temperature of between 80 and 250°C.

17. A process in accordance with any one of claims 9 to 16 wherein the amount of nickel metal ranges from 5 to 60 grams/litre and the amount of copper ranges from 0.2 to 12 grams/litre.

18. A process in accordance with any one of claims 9 to 17 wherein the comingled reaction mixture is heated to boiling point.

19. A process for making a copper promoted nickel silica catalyst in accordance with claim 9 substantially as hereinbefore described with reference to any one of the Examples.

20. A catalyst whenever produced by the process in accordance with any one of claims 9 to 19.

21. A process for hydrogenating an organic compound which comprises contacting at least one hydrogenatable organic compound with hydrogen in the presence of a reduced copper nickel silica catalyst in accordance with claim 8 or claim 20.

22. A process in accordance with claim 21 wherein said hydrogenation is conducted at a temperature ranging from 75°C to 450°C, at a pressure ranging from 1 atmosphere to 12,000 psig, at a space velocity feed rate ranging from 0.2 to 100 V/Hr/V and at a H_2 rate ranging from 2000 to 10,000 SCF/B.

23. A process in accordance with either of claims 21 and 22 wherein at least one of the organic compounds in benzene.

24. A process in accordance with either of claims 21 and 22 wherein at least one of the organic compounds is an aldehyde.

25. A process in accordance with either of claims 21 and 22 wherein the organic compounds include a mixture of a paraffin and at least one olefin.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.