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(54) **CATALYST FOR THE PRODUCTION OF
POLYOLS BY HYDROGENOLYSIS OF
CARBOHYDRATES**

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(57) **ABSTRACT**

A catalyst for the hydrogenolysis of carbohydrates is disclosed. The catalyst comprises nickel metal on an alumina-silica support. Optionally, the catalyst may be promoted with noble metals selected from the group consisting of copper, ruthenium, rhodium, palladium, platinum, gold, silver, and combinations thereof.

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CATALYST FOR THE PRODUCTION OF POLYOLS BY HYDROGENOLYSIS OF CARBOHYDRATES

BACKGROUND

[0001] The present development is a catalyst useful for the production of polyols. Specifically, the invention is directed to the use of a nickel on alumina-silica catalyst for the hydrogenolysis of carbohydrates. Optionally, the catalyst may be promoted with noble metals.

[0002] Polyols are commonly derived from sugars or carbohydrates. An aqueous solution of sugar is treated with hydrogen in the presence of a nickel catalyst to produce a sugar alcohol. The sugar alcohol, when further treated with hydrogen in the presence of the nickel catalyst, can be converted to polyols and glycols.

[0003] Because the media for these hydrogenation reactions is water, it can be challenging to identify an effective, relatively long-lived catalyst for these processes. One approach identified in the prior art was to use colloidal metal. This avoided the problem that many common catalyst supports are not stable in water. However, it was difficult and expensive to remove the colloidal metal from the resulting polyols and glycols. In U.S. Pat. No. 5,162, 517 (issued to Darsow on Nov. 10, 1992), carrier-free catalysts are processed into mouldings from metal powders. The metal powders include elements of the iron group, such as nickel, cobalt, iron and mixtures and alloys of these metals. The mouldings comprise at least 70% metal.

[0004] Supported metal catalysts have also been proposed for use in carbohydrate hydrogenation processes. Silica-alumina carriers are known in the art, but the '517 patent found these to be problematic: "nickel catalysts on a carrier ($\text{SiO}_2/\text{Al}_2\text{O}_3$) [have] extremely high active surfaces of 140-180 m^2/g so that the catalysts are so active that they must be stabilized by additional chemical treatment methods However, the deactivating stabilization of the catalyst then requires such high reaction temperatures during the hydrogenation of sugars (130-180° C.) that uncontrollable side reactions can occur . . ." In U.S. Pat. No. 4,382,150 (issued to Arena on May 3, 1983), the catalyst proposed is a zerovalent Group VIII metal dispersed on titanium dioxide: "whereas substantial amounts of silica and alumina, which are to (sic) commonly employed support materials, dissolve in the aqueous medium during hydrogenation of carbohydrates, virtually no leaching of titanium dioxide occurs under comparable hydrogenation conditions."

[0005] Raney catalysts are known in the art of carbohydrate conversion. For example, U.S. Pat. No. 6,414,201 (issued to Shimazu et al. on Jul. 2, 2002), teaches and claims a process that uses a Raney catalyst formed by melting a mixture of nickel and aluminum and then quenching droplets of the mixture to form a lump alloy, from which particles are broken. However, it is generally known in the art that Raney catalysts work well in static operations, but are not well-adapted to function effectively in continuous processes. Further, similar to the processes using colloid metal, Raney catalysts must be separated and recovered from the reaction mixture at the end of the process.

SUMMARY OF THE INVENTION

[0006] The present development is a catalyst for the hydrogenolysis of carbohydrates comprising nickel metal on

an alumina-silica support. Optionally, the catalyst may be promoted with noble metals. In particular, the catalyst of the present invention comprises from about 45 wt % to about 55 wt % nickel, from about 40 wt % to about 50 wt % alumina, and from about 1 wt % to about 10 wt % silica. The catalyst may further comprise up to about 0.5 wt % promoter.

[0007] The catalyst is intended to be used in an aqueous medium process for converting carbohydrates to polyols and/or glycols. Further, the catalyst is intended to be used as a fixed bed of catalyst in a continuous process for converting carbohydrates to polyol and/or glycols.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0008] The present development is a catalyst for use in processes for converting carbohydrates to polyols and glycols. The carbohydrates are treated with hydrogen in an aqueous medium and in the presence of a hydrogenation catalyst comprising nickel metal on an alumina and silica support. Optionally, the catalyst may be promoted with a noble metal.

[0009] The catalyst of the present invention comprises nickel metal, alumina and silica. The nickel metal comprises from about 45 wt % to about 55 wt % of the total catalyst weight. The alumina to silica ratio preferably ranges from about 4:1 to about 50:1, with the alumina comprising from about 40 wt % to about 50 wt % of the total catalyst weight, and the silica comprising from about 1 wt % to about 10 wt % of the total catalyst weight. In an exemplary embodiment of the catalyst, the nickel comprises from about 48 wt % to about 53 wt % of the total catalyst weight, the alumina comprises from about 43 wt % to about 46 wt % of the total catalyst weight, and the silica comprises from about 1 wt % to about 10 wt % of the total catalyst weight.

[0010] The pore volume of the catalyst is preferably at least about 0.33 cm^3/g , and the specific surface area, measured by the BET procedure, is preferably at least 150 m^2/g . In an exemplary embodiment, greater than about 45% of the volume of the catalyst has a pore size of less than about 100 Å and greater than about 40% of the volume of the catalyst has a pore size of from about 100 Å to about 300 Å.

[0011] The nickel is introduced to the catalyst in the form of nickel nitrate. In an exemplary embodiment, the nickel nitrate is in the form of a solution containing about 13.8 wt % nickel. The alumina is introduced to the catalyst in the form of aluminum nitrate. In an exemplary embodiment, the aluminum nitrate is in the form of a solution containing about 60 wt % solids. The silica is introduced to the catalyst typically as a silica-containing binder in a variety of forms that are known in the art, such as precipitated silica, high surface area silica, bentonite, montmorillonite, and attapulgite.

[0012] In an exemplary process, the catalyst is prepared by a coprecipitation method. The nickel nitrate and aluminum nitrate are added together to form a pre-mix. Soda ash is then added to the pre-mix, and the mixture is allowed to precipitate and age for a period of time. The resulting precipitate is thoroughly washed, dried, and then calcined to an oxide lump. The lump is further ground and mixed with a silica-containing binder. The resulting ground lump is formed into the desired extrusions or tablets. The resulting catalyst

comprises about 50.6 wt % Ni, 44.2 wt % Al_2O_3 , and 5.2 wt % SiO_2 , and has a pore volume of $0.44 \text{ cm}^3/\text{g}$, a BET specific surface area of $161 \text{ m}^2/\text{g}$, and a loss of ignition at 540° C . of less than about 5%.

[0013] Optionally, the catalyst may comprise up to about 0.5 wt % of a metal promoter, such as copper, ruthenium, rhodium, palladium, platinum, gold, silver. The promoter is may be added during precipitation or may be added into the premix—methods that are known in the art.

[0014] The catalyst of the present invention is intended for use in the hydrogenolysis of carbohydrates in aqueous media. The catalyst differs from the catalysts of the prior art by requiring that nickel metal be supported on a predominantly alumina-based support. It is understood that the composition of the catalyst and the specific processing conditions may be varied without exceeding the scope of this development.

1. A catalyst for use in a process for converting carbohydrates to polyols and/or glycols, said process having an aqueous medium, and said catalyst consisting essentially of from about 45 wt % to about 55 wt % nickel and up to about 0.5 wt % of a metal promoter, selected from the group copper, ruthenium, rhodium, palladium, platinum, gold, silver and combinations thereof, wherein said nickel and said promoter are supported on a support comprising from about 40 wt % to about 50 wt % alumina and from about 1 wt % to about 10 wt % silica, wherein the ratio of alumina to silica (Al:Si) is from about 4:1 to about 50:1.

2. (canceled)

3. The catalyst of claim 1 wherein said catalyst comprises from about 48 wt % to about 53 wt % nickel, from about 43 wt % to about 46 wt % alumina, and from about 1 wt % to about 10 wt % silica.

4. (canceled)

5. (canceled)

6. The catalyst of claim 1 wherein said catalyst has a pore volume of at least about $0.33 \text{ cm}^3/\text{g}$.

7. The catalyst of claim 1 wherein said catalyst has a specific surface area, measured by the BET procedure, of at least $150 \text{ m}^2/\text{g}$.

8. The catalyst of claim 1 wherein said nickel is introduced to said catalyst in the form of nickel nitrate, said alumina is introduced to said catalyst in the form of aluminum nitrate, and said silica is introduced to said catalyst as precipitated silica or high surface area silica or bentonite or montmorillonite or attapulgite.

9. The catalyst of claim 9 wherein said nickel nitrate and aluminum nitrate are added together to form a pre-mix to which said promoter is added and then said soda ash is then added the soda ash/pre-mix mixture is allowed to form a precipitate which ages for a predetermined period of time

and then the precipitate is thoroughly wash and dried, and then calcined to form an oxide lump which is further ground and mixed with said silica before being formed into predetermined shapes.

10. A catalyst for converting carbohydrates to polyols and/or glycols, said catalyst comprising from about 45 wt % to about 55 wt % nickel metal, from about 40 wt % to about 50 wt % alumina, and from about 1 wt % to about 10 wt % silica, wherein the ratio of alumina to silica (Al:Si) is from about 4:1 to about 50:1.

11. The catalyst of claim 10 further comprising up to about 0.5 wt % of a metal promoter, selected from the group consisting of copper, ruthenium, rhodium, palladium, platinum, gold, silver and combinations thereof.

12. (canceled)

13. The catalyst of claim 10 wherein said silica is selected from the group consisting of precipitated silica, high surface area silica, bentonite, montmorillonite, attapulgite or combinations thereof.

14. A catalyst for converting carbohydrates to polyols and/or glycols, said catalyst comprising from about 45 wt % to about 55 wt % nickel metal, from about 40 wt % to about 50 wt % alumina, and from about 1 wt % to about 10 wt % silica, and wherein said catalyst is prepared by mixing nickel nitrate and aluminum nitrate together to form a pre-mix to which soda ash is then added, then the soda ash/pre-mix mixture is allowed to form a precipitate which ages for a predetermined period of time, and then the precipitate is thoroughly washed and dried, and then calcined to form an oxide lump which is further ground and mixed with said silica before being formed into predetermined shapes.

15. The catalyst of claim 14 further comprising up to about 0.5 wt % of a metal promoter selected from the group consisting of copper, ruthenium, rhodium, palladium, platinum, gold, silver, and combinations thereof wherein said promoter is added concurrent with the soda ash.

16. The catalyst of claim 14 further comprising up to about 0.5 wt % of a metal promoter selected from the group consisting of copper, ruthenium, rhodium, palladium, platinum, gold, silver, and combinations thereof wherein said promoter is added before the soda ash.

17. The catalyst of claim 8 wherein said nickel nitrate and aluminum nitrate are added together to form a pre-mix mixture to which said promoter and said soda ash is then added concurrently, the soda ash/pre-mix mixture is allowed to form a precipitate which ages for a predetermined period of time, and then the precipitate is thoroughly washed and dried, and then calcined to form an oxide lump which is further ground and mixed with said silica before being formed into predetermined shapes.

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