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DESCRIPTION

Technical Field

[0001] The present development is a catalyst for use in water gas shift processes. The catalyst comprises iron oxide, copper oxide, zinc oxide and alumina, and optionally, potassium oxide.

[0002] The water-gas-shift reaction is a well-known reaction suitable for production of hydrogen. Large volumes of hydrogen gas are needed for a number of important chemical reactions, and since the early 1940's, the water-gas-shift (WGS) reaction has represented an important step in the industrial production of hydrogen. For example, the industrial scale water-gas-shift reaction is used to increase the production of hydrogen for refinery hydro-processes and for use in the production of bulk chemicals such as ammonia, methanol, and alternative hydrocarbon fuels.

[0003] Typically, the catalysts used in the industrial scale water-gas-shift reaction include either an iron-chromium (Fe-Cr) metal combination or a copper-zinc (Cu-Zn) metal combination. The Fe-Cr oxide catalyst is typically used in industrial high temperature shift (HTS) converters. The industrial HTS converters - which have reactor inlet temperatures of from about 300°C to about 380°C - exclusively use the Fe-based catalysts because of their excellent thermal and physical stability, poison resistance and good selectivity. These attributes are especially beneficial when low steam to CO ratios are used and the formation of hydrocarbons is favored. Typically, the commercial catalysts are supplied in the form of pellets containing 8 - 12% Cr₂O₃ and a small amount of copper as an activity and selectivity enhancer. However, because of governmental regulations that pertain to chromium-comprising catalysts, it would be advantageous to have a water gas shift catalyst that demonstrates all the benefits of the prior art Fe-Cr catalyst but which does not require chromium in the composition.

[0004] The copper-based catalysts function well in systems where the CO₂ partial pressure can affect the catalyst performance, so the copper-based catalysts tend to demonstrate more favorable CO conversion at lower temperatures. However, unsupported metallic copper catalysts or copper supported on Al₂O₃, SiO₂, MgO, pumice or Cr₂O₃ tend to have relatively short lifespan (six to nine months) and low space velocity operation (400 to 1000 h⁻¹). The addition of ZnO or ZnO-Al₂O₃ can increase the lifetime of the copper-based catalysts, but the resultant Cu-Zn catalysts generally function in a limited temperature range of from about 200°C to about 300°C. Further, Cu-Zn catalysts tend to be susceptible to poisoning by sulfur-containing compounds. Thus, merely using a Cu-based catalyst or a Cu-Zn catalyst in water gas shift processes is not a viable commercial option.

[0005] WO 02/043734 relates to an iron-based Fischer-Tropsch catalyst composition wherein the main iron phase is ferrihydrite and wherein the catalyst composition includes alumina as a structural promoter. WO 02/043734 also relates to a process for preparing this catalyst. The

use of alumina as a structural promoter in an iron-based catalyst composition wherein the main iron phase is ferrihydrite increases the activity and selectivity of the catalyst by 1.5 to 3 times.

[0006] US 2004/106517 relates to an iron-based Fischer-Tropsch catalyst composition wherein the iron phase is ferrihydrite. The catalyst composition optionally includes a structural promoter which may be selected from manganese or chromium or a mixture thereof and chemical promoters selected from magnesium, zinc, copper and an alkaline or alkali metal such as potassium. The catalyst is best bound to a refractory oxide support such as silica. This catalyst composition produces significant yields of higher paraffins, olefins and alcohols.

[0007] Thus, there is a need for a stable chromium-free iron-based water gas shift catalyst that performs as well as or better than the prior art iron-chromium catalysts.

Summary of the Present Invention

[0008] The present development is a catalyst for use in water gas shift processes, a method for making the catalyst and a method of using the catalyst. The catalyst and method of the invention are set out in the attached claims and consist essentially of iron oxide, copper oxide, zinc oxide and alumina, and optionally, potassium oxide. The catalyst demonstrates surprising activity for conversion of carbon monoxide under high to moderate temperature shift reaction conditions, particularly when the reactor inlet temperatures ranges from about 250°C to about 370°C.

[0009] The disclosure further comprises a process for the production of an Fe_2O_3 / CuO / $\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst. The catalyst is produced using a hydrothermal synthesis process. The process comprises combining salts of iron, copper, zinc and aluminum with an aqueous base solution while maintaining tight control of the reaction temperatures and pH.

Detailed Description of the Invention

[0010] The present development is an Fe_2O_3 / CuO / $\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst intended to be used in water gas shift processes. Specifically, the catalyst of the invention consists essentially of from 0.5 wt% to 15 wt% CuO , from 0.1 wt% to 15 wt% ZnO , from 0.5 wt% to 10 wt% Al_2O_3 , and Fe_2O_3 to balance. (For the purposes of this writing, wt% is based on total weight of the finished catalyst.) In a preferred embodiment, the catalyst consists essentially of from 1.5 wt% to 10 wt% CuO , from 1.5 wt% to 10 wt% ZnO , from 2.0 wt% to 8 wt% Al_2O_3 , and Fe_2O_3 to balance. In a most preferred embodiment, the catalyst consists essentially of from 3.5 wt% to 5.0 wt% CuO , from 3.0 wt% to 5.0 wt% ZnO , from 4.0 wt% to 6.0 wt% Al_2O_3 , and Fe_2O_3 to balance. Optionally, potassium oxide may be included at concentrations up to 5 wt%, and preferably at a concentration of 0.1 wt% to 2.0 wt%, and most preferably at a concentration of 0.2 wt% to 1.0

wt%. The catalyst of the invention is obtainable by the steps:

1. (a) preparing a first solution comprising salts of iron compounds, copper compounds, zinc compounds and aluminum compounds, and by preparing a second solution comprising an aqueous base solution,
2. (b) combining the first and second solutions with deionized water in a mix tank while maintaining the pH,
3. (c) holding the mixture for a predetermined time period, then heating the mixture and holding the mixture at an elevated temperature until solids form;
4. (d) washing the solids,
5. (e) optionally adding potassium compounds
6. (f) drying the washed solids, and
7. (g) calcining the dried solids to make the catalyst.

[0011] The method for preparing the catalyst does not provide for the addition of any chromium-containing materials, but chromium traces may be present, for example, in iron salts of technical purity and thus must be tolerated in the production of the catalysts according to the invention on a technical scale. Further, the method for preparing the catalyst does not provide for the addition of a zinc-aluminum spinel, nor does the method of preparation allow for a zinc-aluminum spinel to form. Thus, the finished catalyst is essentially free of zinc-aluminum spinel as determined by X-Ray Diffraction (XRD).

[0012] The catalyst of the present invention is obtainable, optionally prepared, by first preparing a first solution comprising soluble iron, copper, zinc and aluminum salts. A second basic solution is also prepared. The two solutions are then combined with deionized water in a mix tank optionally at a predetermined temperature of less than about 65°C while maintaining the pH of optionally 4.0 - 12.0. After the solutions are combined, the mixture is held at a predetermined temperature of optionally up to about 100°C for a predetermined time period. The mixture is then heated and held at the elevated temperature optionally for several hours. The solids are washed, dried, and then calcined optionally at 400°C ± 100°C for several hours. In an alternative embodiment, the second basic solution may be added to the water in the mix tank before the addition of the iron solution. In general, the precipitation step may be performed using co-precipitation, acid to base precipitation, or base to acid precipitation methods as are known in the art.

[0013] The soluble metal salts may include nitrate salts, sulfate salts, acetate salts, amine complexes, chloride salts, and other organic and inorganic salts known in the art to deliver iron, copper, zinc and / or aluminum to catalysts. The aluminum may further be added in the form of aluminum oxide, aluminum hydroxide, sodium aluminate and other aluminum compounds that are known in the art for addition of aluminum to catalysts. The basic solution may be prepared from sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, ammonium hydroxide, ammonium carbonates, and other compounds known to produce basic aqueous solutions.

[0014] The resulting catalyst has a BET surface area of 50 - 150 m²/g and a pore volume of 0.15 - 0.45 cc/g.

[0015] The following are representative examples for making the catalyst of the present development. These examples are presented to further explain the invention and are not intended, or to be taken, to limit the scope of the invention.

[0016] Example 1: A catalyst is prepared according to the invention by the following procedure: Ferrous sulfate heptahydrate (145 g) is dissolved in de-ionized (D.I.) water (365 ml). Aluminum nitrate nonahydrate (10.5g) is dissolved in D.I. water (40 ml). The ferrous sulfate heptahydrate solution and the aluminum nitrate nonahydrate solution are combined, and 15.5% Cu (11.8 g) and 15.5% Zn (5.2 g) nitrate solutions are mixed with the ferrous sulfate and aluminum nitrate solutions. The mixed solution is then added into 10% NaOH solution (550 ml) over a 30 minute period, with stirring. The solution is heated to about 65°C and held for at least two hours. The resulting suspension is filtered. The precipitate is washed 4 times with D.I. water followed by drying at 110°C for about four hours. The dried powder is calcined at about 400°C for approximately three hours and the powder is then mixed with 1.5 g graphite. The mixed powders are tabbed.

[0017] Example 2: A catalyst is prepared according to the invention by the following procedure: 10.2% ferrous nitrate solution (2190 g), 15.5% Cu nitrate solution (96 g), 15.5% Zn nitrate solution (32 g) and 4.5% Al nitrate solution (236 g) are mixed in a 3000ml beaker. The mixed solution is added into 20% NH₄OH solution (350ml) over about a 10 minute period, with stirring, followed by heating to about 85°C and holding at temperature for about two hours. The resulting suspension is filtered. The precipitate is washed three times with D.I. water. 4.7 g potassium nitrate solution (43%) is added into the cake. The cake is then dried at 110°C for about four hours followed by calcination at about 300°C for approximately four hours. The calcined powder is mixed with 20g graphite and tabbed.

[0018] Example 3: A catalyst is prepared according to the invention by the following procedure: 357 ml Cu amine (0.14g/l), 143 ml Zn amine (0.14g/l) and 83 g alumina powder are added into about 1900 ml NH₄OH solution (0.2g/ml). After stirring thoroughly, 6154 ml ferrous nitrate solution (0.13g/ml) is added to the NH₄OH solution. The suspension is then heated to about 80°C and held for six hours. After washing and filtrating four times, 6.44g potassium nitrate and 30g graphite are mixed into the slurry. The slurry then is spray-dried followed by calcination with rotation furnace (zone-1, 260°C and zone-2, 350°C). The calcined powder is tabbed.

[0019] Example 4: A catalyst is prepared according to the invention by the following procedure: Ferric nitrate nonahydrate (221 g) is dissolved in 720 ml D.I. water. 15.5% Cu nitrate solution (12.9g), 15.5% Zn nitrate solution (6.5g) and aluminum nitrate powder (18.3g) are added into the ferric nitrate solution. Then the mixed solution is pumped into a precipitation

tank containing 250 ml NaOH solution (25%). The precipitation tank is heated to 60°C and held for 5 hours. The resulting suspension is filtered and washed four times. The cake is dried at 110°C for 3 hours followed by calcination at 400°C for four hours. The calcined powder is then tabbed.

[0020] Example 5: A catalyst is prepared according to the invention by the following procedure: Ferric sulfate (75.4g) is dissolved in 500 ml D.I. water. Ferrous sulfate (41.8g) is dissolved in 122 ml D.I. water. 10.5g aluminum nitrate is dissolved in 35 ml D.I. water. The ferric sulfate, ferrous sulfate and aluminum nitrate solutions are mixed in a first vessel, and a 15.5% Cu nitrate (13 g) solution and 15.5% Zn nitrate (5 g) solution are also mixed into the first vessel. 10% NaOH (500ml) is prepared in second vessel. The solutions from the first vessel and second vessel are added simultaneously to a precipitation tank over about a 30 minute period. The temperature is increased to 65°C and held for about two hours. The resulting suspension is filtered and washed four times with D.I. water followed by drying at 110°C for about four hours. The dried powder is calcined at 400°C for three hours before mixed with 1.5 g graphite.

[0021] Example 6: A catalyst is prepared according to the invention by the following procedure: 55 g aluminum nitrate is dissolved in 180 ml D.I. water. 34 g Cu nitrate solution (15.5%) and 20 g Zn nitrate solution (15.5%) along with the above aluminum nitrate solution are added into 962 g ferrous nitrate solution (9.5%). The mixed solution and 300 ml NaOH solution (25%) are simultaneously added into a precipitation tank with stirring over a 40 minute period. The temperature is then increased to 65°C and held for five hours. The resulting suspension is filtered and washed four times with D.I. water followed by drying at 110°C for four hours. The dried powder is calcined at 400°C for three hours before mixed with 4.5 g graphite. The mixed powders are tabbed.

[0022] Example 7: A catalyst is prepared according to the invention by essentially the same procedure as in Example 6 except 82.5g aluminum nitrate and no Zn nitrate solution are used.

[0023] Example 8: A catalyst is prepared according to the invention by essentially the same procedure as in Example 6 except 51g Cu nitrate solution (15.5%) and no Zn nitrate solution are used.

[0024] The catalyst is preferably used in a typical water gas shift process. Typical reaction conditions for the process would include inlet temperatures equal to or greater than 200°C, feed pressure equal to or greater than 1 atm, and a space velocity greater than about 1000/hr, and a steam to gas ratio of greater than 0.2. The concentration of the carbon monoxide in the feed gas can vary depending on the technical process of producing the gas to be converted. The exit carbon monoxide concentration is expected to be at equilibrium.

[0025] In the water gas shift process, the chromium-free iron-based catalyst of the present invention demonstrates surprisingly improved activity and CO conversion as compared to prior art Fe-Cr catalysts designed for the same purpose. In an exemplary embodiment of the

present invention, the catalyst of Example 6 is prepared. The resulting catalyst has a BET surface area of 67 m²/g and a pore volume of 0.28 cc/g. A prior art catalyst is prepared according to U.S. Patent 7,037,876 Example 1, and comprising about 8 wt% Cr₂O₃ and 2.5 wt% CuO and 89.5 wt% Fe₂O₃. The resulting catalyst has a BET surface area of 75 m²/g and a pore volume of 0.26 cc/g.

[0026] Each catalyst is packed in a fixed bed reactor having an inlet temperature that can be adjusted from 250°C to 370°C. A dry feed comprising 8% CO, 13% CO₂, 24% N₂ and balanced with H₂ is fed through the catalyst bed at a pressure of 10.3 barg (150 psig) and a steam to gas ratio of 0.6. The CO conversion is measured for each catalyst at varying inlet temperatures ranging from 250°C to 370°C. As indicated in Table I, the inventive catalyst demonstrates significantly greater CO conversion at every inlet temperature tested.

Table I

Inlet Temp (°C)	Prior Art Catalyst % CO Conversion	Inventive Catalyst % CO Conversion
250	3	28
275	3	35
300	9	58
325	23	69
370	42	70

[0027] Using the same catalyst compositions, the activity is measured at 370°C for the fresh catalyst and for the same catalysts after the catalyst has been heat treated for 24 hours at 530°C. The fresh prior art catalyst has a CO conversion of 42%, which decreases to 29% after heat treatment. Even with heat treatment the inventive catalyst retains greater activity: the fresh inventive catalyst has a CO conversion of 70%, which decreases to 43% after heat treatment.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO02043734A [0005] [0005]
- US2004106517A [0006]
- US7037876B [0025]

Patentkrav

1. Katalysator, der i det væsentlige består af fra 0,5 vægt-% til 15 vægt-% CuO, fra 0,1 vægt-% til 15 vægt-% ZnO, fra 0,5 vægt-% til 10 vægt-%, Al₂O₃ og valgfrit op til 5 vægt-% K₂O, idet Fe₂O₃ udgør resten, hvor katalysatoren kan opnås ved følgende trin:

- (a) fremstilling af en første opløsning, der omfatter salte af jernforbindelser, kobberforbindelser, zinkforbindelser og aluminiumforbindelser, og ved fremstilling af en anden opløsning, der omfatter en vandig baseopløsning,
- (b) kombination af den første og den anden opløsning med deioniseret vand i en blandetank, mens pH-værdien opretholdes,
- (c) fastholdelse af blandingen i et forudbestemt tidsrum, derefter opvarmning af blandingen og fastholdelse af blandingen ved en forhøjet temperatur, indtil der dannes faststoffer;
- (d) vaskning af faststofferne,
- (e) valgfri tilsætning af kaliumforbindelser
- (f) tørring af de vaskede faststoffer og
- (g) kalcinering af de tørrede faststoffer til fremstilling af katalysatoren.

2. Katalysator ifølge krav 1, der i det væsentlige består af fra 1,5 vægt-% til 10 vægt-% CuO, fra 1,5 vægt-% til 10 vægt-% ZnO, fra 2,0 vægt-% til 8 vægt-% Al₂O₃ og fra 0,1 vægt-% til 2,0 vægt-% K₂O.

3. Katalysator ifølge kravene 1 eller 2, der i det væsentlige består af fra 3,5 vægt-% til 5,0 vægt-% CuO, fra 3,0 vægt-% til 5,0 vægt-% ZnO, fra 4,0 vægt-% til 6,0 vægt-% Al₂O₃ og fra 0,2 vægt-% til 1,0 vægt-% K₂O.

4. Katalysator ifølge et hvilket som helst af kravene 1 til 3, hvor katalysatoren er **kendetegnet ved** et fravær af chromholdige råmaterialer under fremstilling.

5. Katalysator ifølge et hvilket som helst af kravene 1 til 4, hvor katalysatoren er **kendetegnet ved** et fravær af zink-aluminium-spinel.

6. Katalysator ifølge et hvilket som helst af kravene 1 til 5, hvor den anden opløsning tilsættes det deioniserede vand, inden den første opløsning tilsættes det deioniserede vand, og den vandige baseopløsning omfatter vand og en base, som er valgt fra gruppen bestående af NaOH, KOH, Na₂CO₃, K₂CO₃, NH₄OH og (NH₄)₂CO₃, NaHCO₃, KHCO₃, NH₄HCO₃ og urinstof.

7. Katalysator ifølge et hvilket som helst af kravene 1 til 5, hvor den første opløsning tilsættes det deioniserede vand, inden den anden opløsning tilsættes det deioniserede vand, og den vandige baseopløsning omfatter vand og en base, som er valgt fra gruppen bestående af NaOH, KOH, Na₂CO₃, K₂CO₃, NH₄OH og (NH₄)₂CO₃, NaHCO₃, KHCO₃, NH₄HCO₃ og urinstof.

8. Katalysator ifølge et hvilket som helst af kravene 1 til 7, hvor saltene af jernforbindelser, kobberforbindelser, zinkforbindelser og aluminiumforbindelser er valgt

fra gruppen bestående af jernnitrater, jernsulfater, jernacetater, jernaminer, jernchlorider, kobbernitrater, kobbersulfater, kobberacetater, kobberaminer, kobberchlorider, zinknitrater, zinksulfater, zinkacetater, zinkaminer, zinkchlorider, aluminiumnitrater, aluminiumsulfater, aluminiumacetater, aluminiumchlorider, aluminiumoxid, aluminiumhydroxid, natriumaluminat og kombinationer deraf.

9. Fremgangsmåde til anvendelse af katalysatoren ifølge et hvilket som helst af kravene 1 til 8 i en vandgasforskydningsfremgangsmåde, hvor katalysatoren er pakket i en fixed bed-reaktor, og hvor en fødestrøm, der omfatter damp, carbonmonoxid, carbondioxid, nitrogen og hydrogen, tilføres katalysatorlejet ved et forudbestemt tryk og med en forudbestemt rumhastighed.