[005] In the hydroconversion process, it is desirable to employ catalyst having sufficient open volume (porosity) for low mass transfer resistance and facilitate efficient through flow of reactors, while at the same the specific area of each catalyst body should be as large as possible to increase exposure of the reactants to the catalyst material. However, a catalyst that is highly porous does not necessarily mean that the catalyst has a lot of surface area. The catalyst may be too porous, having very little in terms of surface area and correspondingly, low catalytic activity in terms of reactive sites.

[006] There is a need for a bulk / unsupported catalyst for use in the hydroconversion of lower grade hydrocarbon with improved performance, i.e., providing high yield conversions with optimum porosity and surface area. There is also a need for a bulk multi-metallic catalyst having sufficient pore volume / size for hydrotreating heavy oil feeds. There is further a need for a bulk / unsupported catalyst providing high yield conversions as well as exhibiting low shrinkage when exposed to high reaction temperatures.

SUMMARY OF THE ~~INVENTION~~DISCLOSURE

[007] In one aspect, the ~~invention~~disclosure relates to a stable bulk multi-metallic catalyst with low volume shrinkage for use in the hydroconversion of hydrocarbon feedstock, the catalyst is formed from a catalyst precursor having a residual geometric volume shrinkage of less than 10% upon exposure to a temperature of at least 100°C for at least 30 minutes, the precursor comprising: at least a Group VIB metal compound; at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; optionally at least a ligating agent; optionally at least a diluent; wherein the catalyst precursor.

[008] In yet another aspect, the ~~invention~~disclosure relates to a method for forming a catalyst from a catalyst precursor having a low volumetric shrinkage, the method comprising: forming a precipitate comprising at least a promoter metal precursor, at least a Group VIB metal precursor, optionally at least a ligating agent, and optionally at least a diluent, wherein the promoter metal precursor is selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; removing at least 50% of liquid from the precipitate forming a filter cake; adding to the filter cake at least one of a shaping aid agent, a pore forming agent, a peptizing agent, a diluent, and

combinations thereof, forming a batch mixture; shaping the batch mixture into a shaped catalyst precursor via any of pelletizing, extrusion, tableting, molding, tumbling, pressing, spraying and spray drying; drying the shaped catalyst precursor at a temperature ranging from 50°C. to 200°C. for about 15 minutes to 12 hours; and sulfiding the shaped catalyst precursor forming the bulk multi-metallic catalyst. The shaped catalyst precursor is measured for volumetric shrinkage before and after sulfiding, showing a volumetric shrinkage of less than 10%.

[009] In one aspect, a process for hydrotreating a hydrocarbon feed under hydroprocessing conditions is provided. The process comprises contacting the hydrocarbon feed with a bulk multi-metallic catalyst prepared by sulfiding a catalyst precursor comprising at least a Group VIB metal compound; at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; optionally at least a ligating agent; optionally at least a diluent; the catalyst precursor after being shaped, having an essentially monomodal pore size distribution with at least 95% of the pores being macropores and a total pore volume of at least 0.08 g/cc.

[010] In one aspect, a catalyst precursor, upon sulfidation, forms a bulk-multimetallic catalyst for hydrotreating a hydrocarbon feed under hydroprocessing conditions is provided. The catalyst precursor comprises at least a Group VIB metal compound; at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; optionally at least a ligating agent; optionally at least a diluent. The catalyst precursor after being shaped, has an essentially monomodal pore size distribution with at least 95% of the pores being macropores and a total pore volume of at least 0.08 g/cc.

[010a] In one aspect, there is provided a catalyst precursor, upon sulfidation, forms a bulk multi-metallic catalyst for hydrotreating a hydrocarbon feed under hydroprocessing conditions, the catalyst precursor comprising:

at least a Group VIB metal compound;

at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof;

optionally at least a ligating agent L;

optionally at least a diluent;

wherein the catalyst precursor has a residual geometric volume shrinkage of less than 12% upon sulfiding at a temperature of at least 100°C for at least 30 minutes.

[010b] In one aspect, there is provided a catalyst precursor, upon sulfidation, forms a bulk multi-metallic catalyst for hydrotreating a hydrocarbon feed under hydroprocessing conditions, the catalyst precursor comprising

at least a Group VIB metal compound; at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; optionally at least a ligating agent L; optionally at least a diluent;

wherein the catalyst precursor has an essentially monomodal pore size distribution with at least 90% of the pores being macropores and a total pore volume of at least 0.08 g/cc.

[010c] In one aspect, there is provided a method for forming a catalyst from a catalyst precursor having a low volumetric shrinkage, the method comprising:

forming a precipitate comprising at least a promoter metal precursor, at least a Group VIB metal precursor, optionally at least a ligating agent, and optionally at least a diluent, wherein the promoter metal precursor is selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof;

removing at least 50% of liquid from the precipitate forming a filter cake;

adding to the filter cake at least one of a shaping aid agent, a pore forming agent, a peptizing agent, a diluent, and combinations thereof, forming a batch mixture;

shaping the batch mixture into a shaped catalyst precursor via any of pelletizing, extrusion, tableting, molding, tumbling, pressing, spraying and spray drying;

drying the shaped catalyst precursor at a temperature ranging from 50°C. to 325°C. for 15 minutes to 12 hours;

sulfiding the shaped catalyst precursor forming the bulk multi-metallic catalyst, wherein the shaped catalyst precursor has a volumetric shrinkage of less than 12% after sulfiding.

[010c] In one aspect, there is provided a process for hydrotreating a hydrocarbon feed under hydroprocessing conditions, the process comprises contacting the hydrocarbon feed with a bulk multi-metallic catalyst prepared by sulfiding a catalyst precursor comprising at least a Group VIB metal compound; at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; optionally at least a ligating agent; optionally at least a diluent; the catalyst precursor before being sulfided, having an essentially monomodal pore size distribution with at least 90% of the pores being macropores and a total pore volume of at least 0.08 g/cc.

[011] In yet another aspect, a process to prepare a bulk multi-metallic catalyst for hydrotreating a hydrocarbon feed is provided. The process comprising: providing at least a Group VIII metal precursor M^{VIB} and at least promoter metal precursor M^{P}, the promoter metal precursor M^{P} is selected from the group of Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; has an oxidation stat^{e} of either +2 or +4; combining the at least a Group VIII and the at least a promoter metal precursor to form a catalyst precursor precipitate in a liquid solution; separating the catalyst precursor precipitate from the liquid solution forming a filter cake; drying the catalyst precursor filter cake by a non-agglomerative drying method,

Claims

1. A catalyst precursor, upon sulfidation, forms a bulk multi-metallic catalyst for hydrotreating a hydrocarbon feed under hydroprocessing conditions, the catalyst precursor comprising:

at least a Group VIB metal compound;

at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof;

optionally at least a ligating agent L;

optionally at least a diluent;

wherein the catalyst precursor has a residual geometric volume shrinkage of less than 12% upon sulfiding at a temperature of at least 100°C for at least 30 minutes.

2. A catalyst precursor, upon sulfidation, forms a bulk multi-metallic catalyst for hydrotreating a hydrocarbon feed under hydroprocessing conditions, the catalyst precursor comprising

at least a Group VIB metal compound; at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; optionally at least a ligating agent L; optionally at least a diluent;

wherein the catalyst precursor has an essentially monomodal pore size distribution with at least 90% of the pores being macropores and a total pore volume of at least 0.08 g/cc.

3. The catalyst precursor of ~~any of~~ claims 1 or 2~~1-2~~, wherein the catalyst precursor is of the formula $A_v[(M^P)\ (OH)_x\ (L)^n{}_y]_z\ (M^{VIB}O_4)$,

wherein A is at least one of an alkali metal cation, an ammonium, an organic ammonium and a phosphonium cation;

M^P is the at least a promoter metal compound, and M^P is selected elected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof;

L is at the least a ligating agent,

M^{VIB} is the at least a Group VIB metal, having an oxidation state of +6;

M^P: M^{VIB} has an atomic ratio of 100:1 to 1:100;

$v - 2 + P * z - x * z + n * y * z = 0$; and $0 \leq y \leq -P/n$; $0 \leq x \leq P$; $0 \leq v \leq 2$; $0 \leq z$.

4. The catalyst precursor of ~~any of~~ claims 1 or ~~2~~ ~~1-2~~, wherein the catalyst precursor is of the formula $(X)_b(Mo)_c(W)_d O_z$; wherein Mo is the Group VIB metal compound, X is the at least a promoter metal selected from the group of Ni and Co, the molar ratio of b: (c+d) is 0.5/1 to 3/1, the molar ratio of c: d is > 0.01/1, and $z = [2b + 6 (c + d)]/2$.

5. The catalyst precursor of ~~any of~~ claims 1 or ~~2~~ ~~1-2~~, wherein the catalyst precursor has a residual geometric volume shrinkage of less than 10% upon sulfiding at temperature of at least 100°C for at least 30 minutes and a total pore volume of at least 0.10 g/cc.

6. The catalyst precursor of ~~any of~~ claims 1 or ~~2~~ ~~1-2~~, wherein the catalyst precursor has an essentially monomodal pore size distribution with at least 95% of the pores being macropores and a compact bulk density of at most 1.6 g/cc.

7. The catalyst precursor of ~~any of~~ claims 1 or ~~2~~ ~~1-2~~, wherein the catalyst precursor has a BET surface area in the range of 40 to 400 m^2/g.

8. The catalyst precursor of ~~any of~~ claims 1 or ~~2~~ ~~1-2~~, wherein upon sulfidation, forms a bulk-multi-metallic catalyst for hydrotreating a hydrocarbon feed having an atmospheric residue boiling point of at least 343°C. (650°F.) with an HDN conversion rate of at least 99%.

9. The catalyst precursor of ~~any of~~ claims 1 or ~~2~~ ~~1-2~~, wherein upon sulfidation, forms a bulk multi-metallic catalyst for hydrotreating a hydrocarbon feed having an atmospheric residue boiling point of at least 371°C. (700°F.) with with an HDN conversion rate of at least 99%.

10. The catalyst precursor of ~~any of~~ claims 1 or ~~2~~ ~~1-2~~, wherein upon sulfidation, forms a bulk-multi-metallic catalyst for hydrotreating a hydrocarbon feed having an average molecular diameter ranging from 0.9 nm to 1.7 nm and an average molecular weight Mn ranging from 300 to 400.

11. The catalyst precursor of claim 3, wherein

M^P is at least a Group VIII metal, M^{VIB} is selected from molybdenum, tungsten, and combinations thereof, and L is at least one of carboxylates, enolates, and combinations thereof;

the optional ligating agent L is selected from carboxylates, carboxylic acids, aldehydes, ketones, aldehydes, hemiacetals, formic acid, acetic acid, propionic acid, maleic acid, malic acid, cluconic acid, fumaric acid, succinic acid, tartaric acid, citric acid, oxalic acid, glyoxylic acid, aspartic acid, alkane sulfonic acids, aryl sulfonic acids, maleate, formate, acetate, propionate, butyrate, pentanoate, hexanoate, dicarboxylate, and combinations thereof; and

the optional at least a diluent is selected from the group of titania, sodium silicate, potassium silicate, silica gels, silica sols, silica gels, hydronium- or ammonium-stabilized silica sols, sodium aluminate, potassium aluminate, aluminum sulfate, aluminum nitrate, magnesium aluminosilicate clay, magnesium metal, magnesium hydroxide, magnesium halides, magnesium sulfate, magnesium nitrate, zirconia, cationic clay, anionic clays, zinc oxide, zinc sulfide, tetraethyl orthosilicate, silicic acid, niobia, and combinations thereof.

12. The catalyst precursor of ~~any of~~ claims 1 or ~~2~~ ~~1-2~~, wherein the catalyst precursor has a surface area in the range of ~~about~~ 40 to 300 m^2/g; a compact bulk density (CBD) of at most 1.6 g/cc; a pore volume of 0.002 to 2.0 cm^3/g; a crush strength of at least ~~about~~ 5 lbs; and an attrition loss of less than 7 wt.%.

13. A method for forming a catalyst from a catalyst precursor having a low volumetric shrinkage, the method comprising:

forming a precipitate comprising at least a promoter metal precursor, at least a Group VIB metal precursor, optionally at least a ligating agent, and optionally at least a

forming a precipitate comprising at least a promoter metal precursor, at least a Group VIB metal precursor, optionally at least a ligating agent, and optionally at least a diluent, wherein the promoter metal precursor is selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof;

removing at least 50% of liquid from the precipitate forming a filter cake;

adding to the filter cake at least one of a shaping aid agent, a pore forming agent, a peptizing agent, a diluent, and combinations thereof, forming a batch mixture;

shaping the batch mixture into a shaped catalyst precursor via any of pelletizing, extrusion, tableting, molding, tumbling, pressing, spraying and spray drying;

drying the shaped catalyst precursor at a temperature ranging from 50°C. to 325°C. for ~~about~~ 15 minutes to 12 hours;

sulfiding the shaped catalyst precursor forming the bulk multi-metallic catalyst,

wherein the shaped catalyst precursor has a volumetric shrinkage of less than 12% after sulfiding.

14. The method for forming a catalyst of claim 13, wherein

the sulfiding of the shaped catalyst precursor is at a temperature ranging from 70°C to 500°C, from 10 minutes to 15 days; and

wherein the shaped catalyst precursor has a volumetric shrinkage of less than 10% after sulfiding.

15. A process for hydrotreating a hydrocarbon feed under hydroprocessing conditions, the process comprises

contacting the hydrocarbon feed with a bulk multi-metallic catalyst prepared by sulfiding a catalyst precursor comprising at least a Group VIB metal compound; at least a promoter metal compound selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof; optionally at least a ligating agent; optionally at least a diluent; the catalyst precursor before being sulfided, having an essentially monomodal pore size distribution with at least 90% of the pores being macropores and a total pore volume of at least 0.08 g/cc.