

Hydroconversion Multi-Metallic Catalyst and Method for Making Thereof

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to US Patent Application Serial No.
5 61/412,765 with a filing date of November 11, 2010. This application claims priority to and benefits from the foregoing, the disclosures of which are incorporated herein by reference.

TECHNICAL FIELD

[002] The petroleum industry increasingly turns to heavy crudes, resids, coals and tar sands, i.e., lower grade hydrocarbon, as sources for feedstocks. The upgrading or refining
10 of these feedstocks is accomplished by treating the feedstocks with hydrogen in the presence of catalysts to effect conversion of at least a portion of the feeds to lower molecular weight hydrocarbons, or to effect the removal of unwanted compounds, or their conversion to less undesirable compounds

[003] Hydroconversion catalysts can be supported or self-supported (unsupported).
15 Supported catalysts usually comprise of at least one Group VIB metal with one or more Group VIII metals as promoters on a refractory support such as alumina. Unsupported (or "bulk") mixed Group VIII and Group VIB metal catalysts and catalyst precursors used for hydroconversion processes are known in the art as disclosed in U.S. Pat. Nos. 2,238,851; 5,841,013; 6,156,695; 6,566,296 and 6,860,987.

[004] In the process of making and using hydrotreating catalysts, a substantial amount of metal residues and wastes are generated in the form of raw and intermediate materials, e.g., in the supernatant generated in the recovery of the catalyst precursor precipitate and discharged in an effluent stream. In some processes for making hydroconversion catalysts, up to 60% of the metal feed such as Ni, Mo, W, etc., may be
25 wasted and discharged in the effluent stream, putting pressure on the downstream waste treatment process. As the environmental impact of waste disposal such as metal-containing waste materials gets more scrutinized, there is a need for improved processes to make hydroconversion catalysts with minimal waste. There is also a need for effective recovery of residual precious metals from reaction effluents for re-use in the process of making
30 hydrotreating catalysts.

SUMMARY

[005] In one aspect, the ~~disclosure~~invention relates to an improved method for forming a bulk hydroprocessing catalyst with minimal metals in the effluent to waste treatment, the method comprising: co-precipitating at reaction conditions at least one of a Group VIB metal

precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds; treating the supernatant by any of chemical precipitation, ion exchange, electro-coagulation, and combinations thereof to generate first effluent stream containing less than 50 mole % of at least one of the metal residuals; recovering at least 80 mole % of the metal ions in at least one of the metal residuals to form a metal precursor feed; sulfiding the catalyst precursor forming the bulk catalyst; and recycling the metal precursor feed to the co-precipitating step.

[006] In one aspect, the disclosure invention relates to a process for forming a bulk hydroprocessing catalyst, the method comprises co-precipitating at reaction conditions at least one of a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a first catalyst precursor and a first supernatant containing a Promoter metal residual and a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds; adding at least a precipitant to the mixture at a molar ratio of added precipitant to metal residuals ranging from 1.5:1 to 20:1 to precipitate at least 50 mole % of metal ions in at least one of the metal residuals, forming a second catalyst precursor; isolating the first and second catalyst precursors forming a second supernatant containing less than 2000 ppm of metal ions; and sulfiding the first and second catalyst precursors forming the bulk catalyst.

[007] In another aspect for an improved method to form a bulk hydroprocessing catalyst composition, the method comprises: co-precipitating at reaction conditions at least one of a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing a Promoter metal residual and a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds; providing at least an exchange resin; contacting the supernatant with the ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be exchanged and bound onto the resin, forming a first effluent stream containing unbound metal residuals; eluting the resin to produce an eluate containing the previously bound metals; recovering at least 80 mole % of metal ions in the unbound metal

residuals in the first effluent stream or at least 80 mole % of previously bound metal ions in the eluate to form at least a metal precursor feed for use in the co-precipitating step; and sulfiding the catalyst precursor forming the bulk catalyst.

[008] In another aspect for an improved method to form a bulk hydroprocessing catalyst composition, the method comprising: co-precipitating at reaction conditions at least one of a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing a Promoter metal residual and a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds; supplying the supernatant to a vessel having a plurality of electrodes having a positive or a negative charge provided by a power supply; reacting the electrodes with at least one of the metal precursors, forming a slurry containing insoluble metal compounds; recovering the insoluble metal compounds, forming a first effluent stream containing less than 20 mole % of at least one of the metal residuals; recovering at least 80 mole % of at least one of the metal residuals from the first effluent stream to form at least a metal precursor feed for use in the co-precipitating step, forming a second effluent stream contains less than 1000 ppm of one of the metal precursors; sulfiding the catalyst precursor forming the bulk catalyst; and recycling the metal precursor feed to the co-precipitating step.

[009] In another aspect, the disclosure invention relates to an improved method to form a bulk hydroprocessing catalyst composition, comprising co-precipitating at reaction conditions at least one of a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds; mixing the supernatant with at least one of an acid, a sulfide-containing compound, a base, and combinations thereof under mixing conditions at a temperature from ambient to 90°C for a sufficient amount of time to precipitate at least 50% of at least one of the metal residuals, wherein the precipitation is carried out at a pre-select pH; isolating the precipitate to recover a first effluent containing less than 50 mole % of at least one of the metal residuals in the supernatant; converting the precipitate into at least a metal precursor feed; recycling the at least a metal precursor feed to the co-precipitating step; and sulfiding the catalyst precursor forming the bulk catalyst.

[010] In another aspect, the ~~disclosure~~invention relates to yet another method to form a bulk hydroprocessing catalyst composition, comprising: co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds; mixing the supernatant with at least an acid, a sulfide-containing compound, a base under mixing conditions at a temperature from ambient to 90°C to adjust its pH; contacting the supernatant with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be exchanged and bound onto the resin, forming a first effluent containing less than 1000 ppm of at least one of the metal residuals; eluting the resin to produce an eluate containing the previously resin-bound metals; recovering at least 80 mole % of the unbound metal residuals in the first effluent stream or at least 80 mole % of the previously resin-bound metals in the eluate to form at least a metal precursor feed; recycling the metal precursor feed to the co-precipitating step; and sulfiding the catalyst precursor forming the bulk catalyst. In one embodiment with a weak acid resin, the resin functions as an anion exchange resin with an acidic supernatant for the recovery of Group VIB metal residuals, and a cation exchange resin with a basic supernatant for the recovery of Promoter metal residuals.

[011] In yet another aspect, the ~~disclosure~~invention relates to a method for forming a hydroprocessing catalyst composition. The method comprises: co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds; mixing the supernatant with at least one of an acid, a sulfide-containing compound, and combinations thereof for a sufficient amount of time to precipitate at least a portion of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a first pre-select pH; isolating the precipitate to recover a first effluent containing less than 50 mole % of metal ions in at least one of the metal residuals in the supernatant; contacting the first effluent with a first chelated ion exchange resin at a second pre-select pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in

the first effluent to be bound onto the resin, forming a second effluent containing less than 1000 ppm of metal ions in at least one of the metal residuals; and contacting the second effluent with a second chelated ion exchange resin at a third pre-select pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent to be bound onto the resin, forming a third effluent containing less than 100 ppm of metal ions in at least one of the metal residuals.

[011a] In one aspect, there is provided a process for forming a hydroprocessing catalyst composition with minimal amount of metals to waste treatment, the method comprises:

co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor, wherein the reaction conditions comprise a temperature between 25-350° C. and at a pressure between 0 to 3000 psig and a pH of 0-12;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in a total amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least a base or an acid for a sufficient amount of time to precipitate at least 50 mole % of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a pre-selected pH;

isolating the precipitate to recover a first effluent containing less than 50 mole % of metal ions in at least one of the metal residuals in the supernatant;

contacting the first effluent with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent to be bound onto the resin, forming a second effluent containing less than 1000 ppm of metal ions of at least one of the metal residuals;

eluting the resin to produce an eluate containing the metal ions previously bound onto the resin; treating the second effluent stream or the eluate to recover at least 80 mol % of the metal ions in the second effluent stream to form at least a metal precursor feed;

recycling the at least a metal precursor feed formed by treating the second effluent stream or the eluate to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst;

wherein an effluent stream from the process to waste treatment contains less than 50 ppm metal ions.

[011b] In one aspect, there is provided a process for forming a hydroprocessing catalyst composition, the method comprises:

co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor, wherein the reaction conditions comprise a temperature between 25-350° C. and at a pressure between 0 to 3000 psig and a pH of 0-12;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least one of a base, an acid, a sulfide-containing compound, and combinations thereof;

contacting the supernatant with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent containing less than 1000 ppm of at least one of the metal residuals;

eluting the resin to produce an eluate stream containing the metal ions previously bound onto the resin;

treating the first effluent stream or the eluate stream to recover at least 80 mol % of the metal ions in the stream to form at least a metal precursor feed;

recycling the at least a metal precursor feed formed by treating the first effluent stream or the eluate to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst.

[011c] In one aspect, there is provided a process for forming a hydroprocessing catalyst composition, the method comprises:

co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor, wherein the reaction conditions comprise a temperature between 25-350° C. and at a pressure between 0 to 3000 psig and a pH of 0-12;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least one of an acid, a sulfide-containing compound, and combinations thereof for a sufficient amount of time to precipitate at least a portion of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a first pre-selected pH;

isolating the precipitate to recover a first effluent stream containing less than 50 mole % of metal ions in at least one of the metal residuals in the supernatant;

contacting the first effluent stream with a first chelated ion exchange resin at a second pre-selected pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent stream to be bound onto the resin, forming a second effluent stream containing less than 1000 ppm of metal ions in at least one of the metal residuals;

contacting the second effluent stream with a second chelated ion exchange resin at a third pre-selected pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent stream to be bound onto the resin, forming a third effluent stream containing less than 100 ppm of metal ions in at least one of the metal residuals.

[011d] In one aspect, there is provided a process for forming a hydroprocessing catalyst composition, the method comprises:

co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor, wherein the reaction conditions comprise a temperature between 25-350° C. and at a pressure between 0 to 3000 psig and a pH of 0-12;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;
contacting the supernatant with a chelated ion exchange resin at a pre-selected pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent containing less than 1000 ppm of metal ions in at least one of the metal residuals;
eluting the resin to produce an eluate stream containing the metal ions previously bound onto the resin;
treating the first effluent stream or the eluate stream to recover at least 80 mol % of the metal ions in the stream to form at least a metal precursor feed;
recycling the at least a metal precursor feed formed by treating the effluent stream or the eluate stream to the co-precipitating step; and
sulfiding the catalyst precursor forming the bulk catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

[012] Figure 1 provides an overview of an embodiment of a process for making a bulk multi-metallic catalyst with minimal loss of metal waste, including steps to recover the metal components.

[013] Figure 2 provides an overview of another embodiment of a process for making a bulk multi-metallic catalyst including a step to recover metals components with the formation of additional (secondary) catalyst precursor.

[014] Figure 3 is a block diagram of an embodiment employing electro-coagulation technology to recover metal components from the supernatant stream of Figure 1.

[015] Figure 4 is a block diagram of yet another embodiment employing electro-coagulation technology to recover metal components.

[016] Figure 5 is a block diagram of an embodiment employing ion-exchange technology to recover metal components from the supernatant stream.

[017] Figure 6 is a block diagram of another embodiment employing ion-exchange technology, a combination of anionic and cationic exchangers, to recover metal components.

[018] Figure 7 is a block diagram of a third embodiment employing ion-exchange technology to recover metal components.

[019] Figure 8 is a block diagram of an embodiment employing both ion-exchange and electro-coagulation to recover metal components.

DETAILED DESCRIPTION

[020] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[021] SCF / BBL (or scf / bbl, or scfb or SCFB) refers to a unit of standard cubic foot of gas (N₂, H₂, etc.) per barrel of hydrocarbon feed.

[022] LHSV means liquid hourly space velocity.

CLAIMS

1. A process for forming a bulk hydroprocessing catalyst with minimal amount of metals to waste treatment, the method comprising:
- 5 co-precipitating at reaction conditions at least one of a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor;
- isolating the catalyst precursor from the mixture, forming a supernatant containing at
- 10 least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;
- treating the supernatant by any of chemical precipitation, ion exchange, electro-coagulation, and combinations thereof to generate at least a metal precursor feed and a first effluent stream containing less than 50 mole % of metal ions in at least one of the metal
- 15 residuals;
- treating the first effluent stream to recover at least 80 mol % of the metal ions in the first effluent stream;
- recycling the at least a metal precursor feed to the co-precipitating step; and
- sulfiding the catalyst precursor forming the bulk catalyst,
- 20 wherein an effluent stream from the process to waste treatment contains less than 50 ppm metal ions.
2. The process of claim 1, further comprising drying the catalyst precursors at a temperature of at least 150°C before the sulfidation step.
- 25 3. The process of claim 1, further comprising drying the catalyst precursors at a temperature of at least 300°C before the sulfidation step.
4. The process of claim 1, further comprising drying the catalyst precursors at a
- 30 temperature of at least 325°C for the catalyst precursor to have the formula $(X)_b(Mo)_c(W)_dO_z$; wherein X is Ni or 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 process of any of claims 1-4, further comprising drying the catalyst precursors at a temperature of at most 200°C for the catalyst precursor to have the formula $A_v[(M^P)(OH)_x(L)^n]_y(M^{VIB}O_4)_z$, wherein

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

M^P is selected from the group of Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, P is oxidation state with M^P having an oxidation state of either +2 or +4 depending on the selection of M^P ,

L is at least a ligating agent L having an charge $n \leq 0$;

10 M^{VIB} is 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

$0 < y \leq -P/n$; $0 < x \leq P$; $0 < v \leq 2$; $0 < z$.

15 6. The process of any of claims 1-4, wherein the sulfiding of the catalyst precursor forming the bulk catalyst is either before or after loading the catalyst precursor into a hydroprocessing reactor.

7. The process of any of claims 1-4, wherein
20 the supernatant is treated in a reactor vessel having a plurality of electrodes having a positive or a negative charge provided by a power supply, and wherein the electrodes react with at least one of the metal residuals, forming a slurry containing insoluble metal compounds.

25 8. The process of any of claims 1-4, further comprising:
recovering the insoluble metal compound from the slurry, forming an effluent stream containing less than 20 mole % of at least one of the metal residuals in the supernatant.

9. The process of any of claims 1-4, further comprising:
30 adding to the effluent stream at least one of an acid, a sulfide-containing compound, a base, and combinations thereof, under mixing conditions for a sufficient amount of time to precipitate at a first pre-selected pH at least a portion of at least one the metal residuals.

10. The process of claim 9, further comprising:

isolating and recovering the precipitate comprising at least a portion of the metal residuals, generating a third effluent stream containing less than 1000 ppm of at least one the metal residuals.

5 11. The process of any of claims 1-4, wherein:

the supernatant is brought in contact with an exchange resin for a sufficient amount of time for at least 50% of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent stream containing unbound metal residuals.

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12. The process of any of claims 1-4, further comprising:

treating the first effluent in a reactor vessel having a plurality of electrodes having a positive or a negative charge provided by a power supply, and wherein the electrodes react with at least one of the metal residuals, forming a slurry containing at least a precipitate;

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isolating the precipitate from the slurry to recover a second effluent containing less than 2000 ppm metals.

13. The process of claim 12, further comprising:

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adding to the second effluent stream at least an additive selected from the group of an acid, a sulfide-containing compound, a base, and combinations thereof, under mixing conditions for a sufficient amount of time to precipitate at a first pre-selected pH at least a portion of the metal residuals, generating a third effluent stream containing less than 1000 ppm metals.

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14. The process of claim 13, further comprising:

eluting the resin to produce an eluate stream containing the metal ions previously bound onto the resin.

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15. The process of claim 14, further comprising:

recovering at least 80 mole % of the unbound metal residuals in the first effluent stream or at least 80 mole % of the metal ions in the eluate stream to form the at least a metal precursor feed.

16. The process of claim 11, wherein at least a cation exchange resin is provided to exchange and bind the metal ions.
17. The process of claim 11, wherein at least an anion exchange resin is provided to
5 exchange and bind the metal ions.
18. The process of claim 11, wherein at least a cation chelating resin is provided to exchange and bind at least 50 mole % of metal ions in the Group VIB metal residual.
- 10 19. The process of claim 18, wherein the cation chelating resin contains an amine functionality group.
20. The process of claim 1, wherein the sulfiding of the catalyst precursor forming the bulk catalyst is either before or after loading the catalyst precursor into a hydroprocessing
15 reactor.
21. The process of claim 11, wherein the Promoter metal residual comprises a nickel compound, the first effluent stream contains less than 50 ppm Ni, and at least 80% of the nickel is exchanged and bound onto the resin.
- 20 22. The process of claim 14, wherein the resin is eluted with at least an acid to form an eluate.
23. The process of claim 14, wherein the Promoter metal residual comprises a nickel
25 compound and wherein the resin is eluted with sulfuric acid to a pH of less than 3, forming $\text{Ni}(\text{NO}_3)_2$ for use in the co-precipitation step as a Promoter metal precursor feed.
24. The process of claim 11, further comprising treating the first effluent stream by chemical precipitation to recover the Group VIB metal residual as a Group VIB metal
30 precursor feed.
25. The process of claim 24, wherein the first effluent stream is treated by adding at least an acid under mixing conditions for a sufficient amount of time to precipitate at a first pre-selected pH at least a portion of the Group VIB metal residual.

26. The process of claim 25, further comprising isolating and recovering the precipitate, forming a second effluent stream comprising less than 25 mole % of the Group VIB metal residual.

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27. The process of claim 26, further comprising adding at least a calcium compound to the second effluent stream under mixing conditions forming at least a calcium salt.

28. The process of claim 27, wherein the molar ratio of added calcium compound to the Group VIB metal residual ranges from 2:1 to 50:1.

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29. A process for forming a bulk hydroprocessing catalyst, the method comprises:
co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a product mixture comprising a first catalyst precursor and a first supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;
adding at least a precipitant to the product mixture at a molar ratio of precipitant to metal residuals in solution ranging from 1.5:1 to 20:1 to precipitate at least 50 mole % of metal ions in the residuals forming additional catalyst precursor;
isolating the catalyst precursors from the product mixture, forming a second supernatant containing less than 5000 ppm of metal ions in the metal residuals; and sulfiding the catalyst precursors forming the bulk catalyst.

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30. The process of claim 29, further comprising drying the first and additional catalyst precursors at a temperature of 150 to 300°C before the sulfidation step.

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31. The process of claim 29, further comprising calcining the first and second catalyst precursors at a temperature of at least 300°C before the sulfidation step.

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32. The process of claim 31, wherein the calcination is at a temperature of at least 325°C to form at least one catalyst precursor having the formula $(X)_b(\text{Mo})_c(\text{W})_d\text{O}_z$; wherein X is Ni or 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 $z = [2b + 6(c + d)]/2$.

33. The process of claim 31, wherein the drying is at a temperature of 200°C or less, forming at least a catalyst precursor having the formula $A_v[(M^P)(OH)_x(L)^n_y]_z(M^{VIB}O_4)$, wherein

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

M^P is selected from the group of Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, P is oxidation state with M^P having an oxidation state of either +2 or +4 depending on the selection of M^P ,

10 L is at least a ligating agent L having an charge $n \leq 0$;

M^{VIB} is 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

$0 < y \leq -P/n$; $0 < x \leq P$; $0 < v \leq 2$; $0 < z$.

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34. The process of claim 35, wherein M^P is at least a Group VIII metal.

35. The process of claim 28, wherein the isolation of the first and additional catalyst precursors is via at least one of filtering, decanting, centrifuging, and combinations thereof.

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36. The process of claim 28, prior to the addition of the precipitant, further comprising adjusting the pH of the mixture to a pre-selected pH to facilitate the formation of the additional catalyst precursor.

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37. The process of claim 28, prior to the isolation of the first and additional catalyst precursors, further comprising adjusting the pH of the mixture to a pre-selected pH to facilitate the isolation of the first and additional catalyst precursors.

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38. The process of claim 37, wherein the pH of the mixture is adjusted by adding at least an acid or a base.

39. The process of claim 38, wherein the pH of the mixture is adjusted by adding nitric acid.

40. The process of claim 39, wherein the pH of the mixture is adjusted to about 5 to 6.5.
41. The process of claim 28, wherein the precipitant is selected from compounds of metals exhibiting amphoteric behavior.
- 5 42. The process of claim 41, wherein the precipitant is selected from compounds of Ni, Zn, Al, Sn, and Nb.
43. The process of claim 42, wherein the precipitant is selected from aluminium nitrate, aluminium sulphate, zinc nitrate, ammonium aluminate, ammonium zincate, niobium
10 pentoxide, zirconium oxide, and mixtures thereof.
44. The process of claim 43, wherein the precipitant is ammonium aluminate.
- 15 45. The process of claim 28, wherein the precipitant is selected from the group of alumina, alumina silica, titanates, silicates and mixtures thereof.
46. The process of claim 28, further comprising:
supplying the second supernatant to a reactor vessel having a plurality of electrodes
20 having a positive or a negative charge provided by a power supply, forming a slurry containing insoluble metal compounds;
recovering the insoluble metal compounds, forming a first effluent stream containing less than 100 ppm metals.
- 25 47. The process of claim 28, further comprising:
providing at least an exchange resin;
contacting the second supernatant with the ion exchange resin for at least 50% of metal ions in at least one of the metal residuals in the second supernatant to be bound onto the resin, forming an effluent stream containing less than 100 ppm metals.
- 30 48. The process of claim 28, further comprising:
treating the second supernatant with at least an additive selected from the group of acids, sulfide-containing compound, bases, and mixtures thereof under mixing conditions for

a sufficient amount of time to precipitate at a pre-selected pH at least a portion of the first and second metal residuals, forming an effluent stream containing less than 100 ppm metals.

49. The process of claim 28, wherein the sulfiding of the first and second catalyst precursors forming the bulk catalyst is either before or after loading the catalyst precursors into a hydroprocessing reactor.

50. A process for forming a hydroprocessing catalyst composition, the method comprises:
co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in a total amount of at least 10 mole % of metal ions in the metal precursor feeds;

contacting the supernatant with an ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in the metal residuals to be bound onto the resin, forming a first effluent stream containing unbound metal residuals;

eluting the resin to produce an eluate stream containing the metals ions previously bound onto the resin;

treating the first effluent stream or the eluate stream to recover at least 80 mol % of metal ions in the stream to form at least a metal precursor feed;

recycling the metal precursor feed to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst.

51. The process of claim 50, wherein the supernatant is contacted with the ion exchange resin for a sufficient amount of time for at least 80 mole % of the metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin.

52. The process of claim 50, wherein at least a cation exchange resin is provided to bind at least 80% of metal ions in the Promoter metal residual.

53. The process of claim 52, wherein the Promoter metal residual comprises a nickel compound, the first effluent stream contains less than 50 ppm Ni, and at least 80% of the nickel is bound onto the resin.

54. The process of claim 50, wherein the resin is eluted with at least an acid to form an eluate.

5 55. The process of claim 54, wherein the Promoter metal residual comprises a nickel compound and wherein the resin is eluted with sulfuric acid to a pH of less than 3, forming $\text{Ni}(\text{SO}_4)$ for use in the co-precipitation step as a Promoter metal precursor feed.

56. The process of claim 50, further comprising treating the first effluent stream by
10 chemical precipitation to recover the unbound metal residuals as a Group VIB metal precursor feed.

57. The process of claim 56, wherein the first effluent is treated by adding at least an acid under mixing conditions for a sufficient amount of time to precipitate at a first pre-selected
15 pH at least a portion of the unbound metal residuals.

58. The process of claim 57, further comprising isolating and recovering the precipitate, forming a second effluent stream comprising less than 25 mole % of the Group VIB metal residual.
20

59. The process of claim 58, further comprising adding at least a calcium compound to the second effluent stream under mixing conditions forming at least a calcium salt.

60. The process of claim 59, wherein the molar ratio of added calcium compound to the
25 Group VIB metal residual ranges from 2:1 to 50:1.

61. The process of claim 60, wherein the Group VIB metal residual comprises at least a molybdenum compound and a tungsten compound and the calcium salt comprises at least one of CaMoO_4 and CaWO_4 .
30

62. The process of claim 58, further comprising acidifying the second effluent stream to a pH of less than 7.

63. The process of claim 58, wherein the Group VIB metal residual comprises at least a molybdenum compound and a tungsten compound and the precipitate comprises molybdate, tungstate and combinations thereof.

5 64. The process of claim 63, further comprising dissolving the precipitate comprising molybdate, tungstate and combinations thereof in an aqueous ammonium hydroxide solution, forming ammonium heptamolybdate, ammonium heptatungstate and combinations thereof.

65. The process of claim 50, wherein at least an anion exchange resin is provided to bind
10 at least 80% of the metal ions in the Group VIB metal residual.

66. The process of claim 50, wherein the resin is eluted with hydroxide based to form an eluate.

15 67. The process of claim 50, wherein at least a cation chelating resin is provided to bind at least 80% of the metal ions in the Group VIB metal residual.

68. The process of claim 67, wherein the cation chelating resin contains an amine functionality group.
20

69. The process of claim 50, further comprising calcining the catalyst precursor at a temperature of at least 300°C before the sulfidation step.

70. The process of claim 69, wherein the calcination is at a temperature of at least 325°C
25 for the catalyst precursor to have the formula $(X)_b(Mo)_c(W)_dO_z$; wherein X is Ni or 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 $z = [2b + 6(c + d)]/2$.

71. The process of claim 50, further comprising drying the catalyst precursor at a
30 temperature of 200°C or less before the sulfidation step for a catalyst precursor with the formula $A_v[(M^P)(OH)_x(L)^n]_y(M^{VIB}O_4)_z$, wherein

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

M^P is selected from the group of Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, P is oxidation state with M^P having an oxidation state of either +2 or +4 depending on the selection of M^P ,

L is at least a ligating agent L having an charge $n \leq 0$;

5 M^{VIB} is 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

$0 < y \leq -P/n$; $0 < x \leq P$; $0 < v \leq 2$; $0 < z$.

10 72. In a process for forming a bulk hydroprocessing catalyst, the process comprising: co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter
15 metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of metal ions in the metal precursor feeds; calcining the catalyst precursor to form a catalyst precursor of the formula $(X)_b(Mo)_c(W)_dO_z$; wherein X is Ni or 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 $z = [2b + 6(c + d)]/2$; and sulfiding the catalyst precursor forming the bulk catalyst, wherein the improvement
20 comprising:

contacting the supernatant with an ion exchange resin for a sufficient amount of time for at least 50% of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent stream containing unbound metal residuals;

25 eluting the resin to produce an eluate stream containing metals ions previously bound onto the resin; and

treating the first effluent stream or the eluate stream to recover at least 80 mol % of metal ions in the stream to form at least a metal precursor feed;

73. A process for forming a hydroprocessing catalyst composition, the method comprises:
30 co-precipitating at reaction conditions at least one of a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10% of the metal precursor feeds;

5 treating the supernatant with at least an acid at a pre-selected pH to precipitate at least a Promoter metal residual and a Group VIB metal residual, forming a first effluent stream containing less than 50% of at least one of Promoter metal residual and a Group VIB metal residual;

providing at least an exchange resin;

10 contacting the supernatant with the ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent stream containing unbound metal residuals;

eluting the resin to produce an eluate containing the metal ions previously bound onto the resin;

15 recovering at least 80 mole % of metal ions in the unbound metal residuals in the first effluent stream or at least 80 mole % of the metal ions in the eluate to form at least a metal precursor feed;

recycling the metal precursor feed to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst.

20 74. The process of claim 73, wherein at least a cation chelating resin is provided to exchange and bind at least 50 mole % of metal ions in the Group VIB metal residual.

75. The process of claim 74, wherein the cation chelating resin contains an amine functionality group.

25

76. The process of claim 50, wherein the supernatant is brought into contact with a chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine.

30 77. The process of claim 50, wherein the first effluent stream or the eluate stream is treated generating an effluent to waste treatment containing less than 50 ppm of Group VIB and Promoter metals.

78. A process for forming a bulk hydroprocessing catalyst with minimal amount of metals to waste treatment, the method comprises:

co-precipitating at reaction conditions at least one of a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor;

- 5 isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in a total amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least one of an acid, a sulfide-containing compound, a base, and combinations thereof under mixing conditions at a temperature from ambient to 10 90°C for a sufficient amount of time to precipitate at least 50 mole % of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a pre-select pH;

isolating the precipitate to recover a first effluent stream containing less than 50 mole % of metal ions in at least one of the metal residuals in the supernatant;

- 15 converting the metal ions in the precipitate or the first effluent stream into at least a metal precursor feed;

recycling the at least a metal precursor feed to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst.

79. The process of claim 78, wherein an effluent stream from the process to waste 20 treatment contains less than 50 ppm metals.

80. The process of claim 78, further comprising drying the catalyst precursors at a temperature of at least 150°C before the sulfidation step.

- 25 81. The process of any of claims 78-80, further comprising drying the catalyst precursors at a temperature of at least 325°C for the catalyst precursor to have the formula $(X)_b(Mo)_c(W)_dO_z$; wherein X is Ni or 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 $z = [2b + 6(c + d)]/2$.

- 30 82. The process of any of claims 78-80, further comprising drying the catalyst precursors at a temperature of at most 200°C and wherein the catalyst precursor has the formula $A_v[(M^P)(OH)_x(L)^n]_y(M^{VIB}O_4)_z$, wherein

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

M^P is selected from the group of Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, P is oxidation state with M^P having an oxidation state of either +2 or +4 depending on the selection of M^P ,

L is at least a ligating agent L having an charge $n \leq 0$;

5 M^{VIB} is 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

$0 < y \leq -P/n$; $0 < x \leq P$; $0 < v \leq 2$; $0 < z$.

10 83. The process of any of claims 78-80, wherein the supernatant is mixed with at least an acid selected from the group of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, acetic acid, oxalic acid, nitric acid, and mixtures thereof.

15 84. The process of claim 83, wherein the acid is nitric acid and the precipitation is carried out at a pH of less than 3.

85. The process of any of claims 78-80, wherein the at least one of a Group VIB metal precursor feed comprises Mo and W compounds and the first effluent stream comprising less than 1000 ppm each of Mo and W.

20 86. The process of any of claims 78-80, wherein converting the metal ions in the precipitate comprises dissolving the precipitate in an aqueous ammonium hydroxide solution, forming at least one of ammonium molybdate and ammonium tungstate as Group VIB metal precursor feeds.

25 87. The process of any of claims 78-80, wherein the at least a Promoter metal precursor feed comprises a Ni compound and wherein converting the metal ions in the first effluent stream comprises treating the first effluent stream with a base for a sufficient amount of time to precipitate the Ni compound, wherein the precipitation is carried out at a pre-selected pH.

30 88. The process of claim 87, wherein the pre-selected pH is at least 7.

89. The process of claim 88, further comprising isolating and recovering the precipitate for a second effluent stream containing less than 20 ppm of Ni.

90. The process of any of claims 78-80, further comprising:

treating the first effluent stream in a reactor vessel having a plurality of electrodes having a positive or a negative charge provided by a power supply, and wherein the electrodes react with at least one of the metal residuals, forming a slurry containing insoluble metal compound;

recovering the insoluble metal compound from the slurry, forming a second effluent containing less than 2000 ppm of at least one of the metal residuals.

10 91. The process of claim 90, further comprising:

adding to the second effluent stream at least an additive selected from the group of an acid, a sulfide-containing compound, a base, and combinations thereof, under mixing conditions for a sufficient amount of time to precipitate at a first pre-selected pH at least a portion of at least one of the metal residuals, generating a third effluent stream containing less than 1000 ppm of metal ions in at least one of the metal residuals.

92. The process any of claims 78-80, further comprising:

treating the first effluent with an exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in first effluent to be bound onto the resin, forming a second effluent stream containing unbound metal residuals.

93. The process of claim 92, further comprising:

eluting the resin to produce an eluate stream containing the metal ions previously bound onto the resin;

treating the second effluent stream or the eluate stream to recover at least 80 mol % of the metal ions in the stream to form at least a metal precursor feed;

94. The process of claim 93, wherein at least 80 mole % of metal ions in the second effluent stream is recovered by adding to the second effluent stream at least one of an acid, a sulfide-containing compound, a base, and combinations thereof, under mixing conditions for a sufficient amount of time to precipitate at a first pre-selected pH at least a portion of at least one of the metal residuals, generating a third effluent stream containing less than 1000 ppm of metal ions in at least one of the metal residuals.

95. The process of any of claims 78-80, further comprising:

running the first effluent through a filtering system having a plurality of filter having a successive decrease in sizes, forming a second effluent containing less than 2000 ppm of metal ions in at least one of the metal residuals.

96. The process any of claims 78-80, wherein an effluent stream from the process to waste treatment contains less than 50 ppm of Group VIB and Promoter metals.

97. In a process for forming a bulk hydroprocessing catalyst, the process comprising: co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds; calcining the catalyst precursor to form a catalyst precursor of the formula $(X)_b(Mo)_c(W)_dO_z$; wherein X is Ni or 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 $z = [2b + 6(c + d)]/2$; and sulfiding the catalyst precursor forming the bulk catalyst, the improvement comprising:

mixing the supernatant with at least one of an acid, a base, and combinations thereof under mixing conditions at a temperature from ambient to 90°C for a sufficient amount of time to precipitate at least 50 mole % of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a pre-select pH;

isolating the precipitate to recover a first effluent containing less than 20 mole % of metal ions in at least one of the metal residuals in the supernatant;

dissolving the precipitate with at least a base to convert the metal ions in the precipitate into at least a metal precursor feed; and

recycling the at least a metal precursor feed to the co-precipitating step.

98. The process of claim 97, further comprising:

treating the first effluent in a reactor vessel having a plurality of electrodes having a positive or a negative charge provided by a power supply, and wherein the electrodes react with at least one of the metal residuals, forming a slurry containing at least a precipitate;

isolating the precipitate from the slurry to recover a second effluent containing less than 5000 ppm of metal ions in at least one of the metal residuals.

99. The process of claim 98, further comprising:

adding to the second effluent stream at least an additive selected from the group of an acid, a sulfide-containing compound, a base, and combinations thereof, under mixing conditions for a sufficient amount of time to precipitate at a first pre-selected pH at least a portion of at least one of the metal residuals, generating a third effluent stream containing less than 1000 ppm of metal ions in at least one of the metal residuals.

100. The process of claim 99, wherein mixing the supernatant comprises mixing the

supernatant with at least an acid selected from the group of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, acetic acid, oxalic acid, nitric acid, and mixtures thereof for a pre-select pH of less than 3.

101. The process of claim 99, wherein the at least one of a Group VIB metal precursor feed comprises Mo and W compounds and the first effluent stream comprising less than 1000 ppm each of Mo and W.

102. A process for forming a hydroprocessing catalyst composition with minimal amount of metals to waste treatment, the method comprises:

co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in a total amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least a base or an acid for a sufficient amount of time to precipitate at least 50 mole % of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a pre-select pH;

isolating the precipitate to recover a first effluent containing less than 50 mole % of metal ions in at least one of the metal residuals in the supernatant;

contacting the first effluent with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent to be bound onto the resin, forming a second effluent containing less than 1000 ppm of metal ions of at least one of the metal residuals;

eluting the resin to produce an eluate containing the metal ions previously bound onto the resin;

treating the second effluent stream or the eluate to recover at least 80 mol % of the metal ions in the second effluent stream to form at least a metal precursor feed;

5 recycling the metal precursor feed to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst;

wherein an effluent stream from the process to waste treatment contains less than 50 ppm metal ions.

10 103. The process of claim 102, wherein the chelated ion exchange resin contains an amine functionality group.

104. The process of claim 102, wherein the chelated ion exchange resin has at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur
15 substituent, amine oxide and hydroxy amine.

105. The process of any of claims 102-104, wherein mixing the supernatant comprises mixing the supernatant with at least an acid selected from the group of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, acetic acid, oxalic acid, nitric acid, and
20 mixtures thereof.

106. The process of claim 105, wherein the acid is nitric acid and the precipitation is carried out at a pH of less than 3.

25 107. The process of any of claims 102-104, wherein the at least one of a Group VIB metal precursor feed comprises Mo and W compounds, the Promoter metal residual comprises Ni, and the first effluent comprises less than 2000 ppm each of Mo, W, and Ni.

108. The process of claim 107, wherein the first effluent stream is brought into contact
30 with a chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine, for the second effluent to have less than 50 ppm each of Mo and W.

109. The process of claim 108, wherein the second effluent is mixed with at least a base selected from the group of ammonium chloride, ammonium citrate, ammonium lactate, potassium hydroxide, potassium formate, sodium hydroxide, sodium acetate, ammonium hydroxide and mixtures thereof, to adjust its pH to a pre-select basic pH.

110. The process of claim 109, wherein the second effluent at a pre-selected basic pH is brought into contact with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of the Ni in the second effluent to be exchanged and bound onto the resin, forming a third effluent containing less than 10 ppm Ni.

111. The process of any of claims 102-104, further comprising drying the catalyst precursors at a temperature of at least 150°C before the sulfidation step.

112. The process of claim 111, wherein the catalyst precursor is dried at a temperature of at least 300°C before the sulfidation step.

113. The process of claim 111, wherein the catalyst precursor is dried at a temperature of at least 325°C for the catalyst precursor to have the formula $(X)_b(Mo)_c(W)_dO_z$; wherein X is Ni or 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 $z = [2b + 6(c + d)]/2$.

114. The process of claim 111, wherein the catalyst precursor is dried at a temperature of at most 200°C for the catalyst precursor to have 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 selected from the group of Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, P is oxidation state with M^P having an oxidation state of either +2 or +4 depending on the selection of M^P ,

L is at least a ligating agent L having a charge $n \leq 0$;

M^{VIB} is 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;

$y - 2 + P * z - x * z + n * y * z = 0$; and

$0 < y \leq -P/n$; $0 < x \leq P$; $0 < v \leq 2$; $0 < z$.

115. The process of any of claims 102-104, wherein the sulfiding of the catalyst precursor forming the bulk catalyst is either before or after loading the catalyst precursor into a hydroprocessing reactor.

5

116. A process for forming a hydroprocessing catalyst composition, the method comprises: co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor;

10 isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least one of an acid, a sulfide-containing compound, and combinations thereof;

15 contacting the supernatant with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent containing less than 1000 ppm of at least one of the metal residuals;

20 eluting the resin to produce an eluate containing the metal ions previously bound onto the resin;

treating the first effluent stream or the eluate to recover at least 80 mol % of the metal ions in the stream to form at least a metal precursor feed;

recycling the metal precursor feed to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst.

25

117. The process of claim 116, wherein the supernatant is mixed with at least an acid selected from the group of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, acetic acid, oxalic acid, nitric acid, and mixtures thereof to adjust its pH to a pre-select acidic pH.

30

118. The process of claim 116, wherein the supernatant is brought into contact with a chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine.

119. The process claim 116, wherein the chelated ion exchange resin functions as an anion exchange resin for at least 50 mole % of at least a Group VIB metal residual in the supernatant to be exchanged and bound onto the resin, forming a first effluent containing less than 1000 ppm of Group VIB metals.

120. The process claim 119, wherein the first effluent is brought into contact with at least a base selected from the group of ammonium chloride, ammonium citrate, ammonium lactate, potassium hydroxide, potassium formate, sodium hydroxide, sodium acetate, ammonium hydroxide and mixtures thereof, to adjust its pH to a pre-select basic pH.

121. The process of claim 120, wherein the first effluent at a pre-select basic pH is brought into contact with a chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine.

122. The process of claim 116, wherein the chelated ion exchange resin functions as an cation exchange resin for at least 50 mole % of at least a Promoter precursor in the first effluent to be exchanged and bound onto the resin, forming a first effluent containing less than 50 ppm of Promoter metals.

123. A process for forming a hydroprocessing catalyst composition, the method comprises: co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least one of an acid, a sulfide-containing compound, and combinations thereof for a sufficient amount of time to precipitate at least a portion of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a first pre-select pH;

isolating the precipitate to recover a first effluent containing less than 50 mole % of metal ions in at least one of the metal residuals in the supernatant;

contacting the first effluent with a first chelated ion exchange resin at a second pre-select pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent to be bound onto the resin, forming a second effluent containing less than 1000 ppm of metal ions in at least one of the metal residuals;

5 contacting the second effluent with a second chelated ion exchange resin at a third pre-select pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent to be bound onto the resin, forming a third effluent containing less than 100 ppm of metal ions in at least one of the metal residuals.

10 124. The method of claim 123, further comprising adding an acid to the first effluent for the first effluent to have a second pre-select pH prior to contacting the first effluent with the first chelated ion exchange resin at the second pre-select pH.

15 125. The method of claim 123, further comprising adding a base to the second effluent for the second effluent to have a third pre-select pH prior to contacting the second effluent with the second chelated ion exchange resin at the third pre-select pH.

20 126. The method of claim 123, wherein the first chelated ion exchange resin and the second chelated ion exchange resin are of the same type.

127. The method of claim 123, wherein the second pre-select pH is acidic for the first chelated ion exchange resin to function as an anion exchange.

25 128. The method of claim 127, wherein the second pre-select pH is 1-2.

129. The method of claim 123, wherein the third pre-selected pH is neutral to basic for the second chelated ion exchange resin to function as a cation exchange.

30 130. The method of claim 129, wherein the third pre-select pH is 6-8.

131. A process for forming a hydroprocessing catalyst composition, the method comprises: co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;

5 contacting the supernatant with a chelated ion exchange resin at a pre-select pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent containing less than 1000 ppm of metal ions in at least one of the metal residuals;

eluting the resin to produce an eluate containing the metal ions previously bound onto the resin;

10 treating the first effluent stream or the eluate to recover at least 80 mol % of the metal ions in the stream to form at least a metal precursor feed;

recycling the metal precursor feed to the co-precipitating step; and
sulfiding the catalyst precursor forming the bulk catalyst.

15 132. The process of claim 131, wherein the supernatant is mixed with at least a base selected from the group of ammonium chloride, ammonium citrate, ammonium lactate, potassium hydroxide, potassium formate, sodium hydroxide, sodium acetate, ammonium hydroxide and mixtures thereof, to adjust its pH to the pre-select pH.

20 133. The process claim 131, wherein the the supernatant is mixed with at least an acid selected from the group of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, acetic acid, nitric acid, and mixtures thereof to adjust its pH to the pre-select pH.

134. The process of claim 131, wherein the supernatant is brought into contact with a
25 chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine.

135. The process claim 131, wherein the chelated ion exchange resin functions as a cation
30 exchange resin for at least 50 mole % of metal ions in at least a Promoter metal residual in the supernatant to be exchanged and bound onto the resin, forming a first effluent containing less than 1000 ppm of Promoter metals.

136. The process of claim 131, wherein the chelated ion exchange resin functions as an anion exchange resin for at least 50 mole % of metal ions in at least a Group VIB metal

residual in the supernatant to be exchanged and bound onto the resin, forming a first effluent containing less than 1000 ppm of Group VIB metals.

137. A process for forming a bulk hydroprocessing catalyst, the method comprises:

- 5 co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor;
- isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in a total amount of
- 10 at least 10 mole % of the metal precursor feeds;
- supplying the supernatant to a reactor vessel having a plurality of electrodes having a positive or a negative charge provided by a power supply, wherein the electrodes dissolve in water generating an electrode dissolution product;
- reacting the electrode dissolution product with at least one of the metal residuals,
- 15 forming a slurry containing insoluble metal compounds;
- isolating the insoluble metal compounds from the slurry, forming a first effluent stream containing less than 50 mole % of metal ions in the metal residuals;
- treating the first effluent stream to recover at least 80 mol % of the metal ions to form at least a metal precursor feed;
- 20 recycling the metal precursor feed to the co-precipitating step; and
- sulfiding the catalyst precursor forming the bulk catalyst.

138. The process of claim 137, wherein the recovering of 80 mole % of at least one of the metal residuals from the first effluent stream comprises treating the first effluent stream by

25 chemical precipitation, forming a second effluent stream contains less than 2000 ppm of at least one of the metal residuals;

139. The process of any of claims 137-138, wherein the electrodes are aluminium.

30 140. The process of claim 139, wherein the electrodes sacrifice aluminium ions into the supernatant forming at least an aluminum complex with at least one of the Promoter metal residual.

141. The process of any of claims 137-138, wherein the Promoter metal residual comprises at least a nickel compound and the insoluble metal compounds comprise NiAlO_4 .

142. The process of any of claims 137-138, wherein the first effluent stream contains less
5 than 20 mole % of the Promoter metal residual.

143. The process of claim 142, wherein the first effluent stream contains less than 50 ppm of the Promoter metal residual.

10 144. The process of any of claims 137-138, wherein the Group VIB metal residual comprises at least a Mo compound and a W compound.

145. The process of any of claims 137-138, wherein the treatment of the first effluent stream comprises adding at least an additive selected from the group of a base, an acid, a
15 sulfide-containing compound, and mixtures thereof under mixing conditions for a sufficient amount of time to precipitate at least a portion of at least one of the metal residuals at a first pre-selected pH.

146. The process of claim 145, wherein the additive is selected from the group of nitric
20 acid and sulphuric acid and the first pre-selected pH is less than 3.

147. The process of claim 145, further comprising isolating and recovering the precipitate forming a second effluent stream comprising less than 25 mole % of at least one of the metal
25 residuals.

148. The process of claim 147, further comprising acidifying the second effluent stream to a pH of less than 6.5.

149. The process of claim 147, further comprising adding at least a calcium compound to
30 the second effluent stream under mixing conditions forming a slurry containing at least a calcium salt, wherein the molar ratio of added calcium compound to Group VIB metal residual is 2/1 to 50/1.

150. The process of claim 149, wherein the calcium salt comprises at least one of CaMoO_4 and CaWO_4 .

151. The process of claim 149, further comprising isolating and recovering the calcium salt, forming an effluent stream containing less than 500 ppm metals.

152. The process of any of claims 137-138, further comprising calcining the catalyst precursor at a temperature of at least 300°C before the sulfidation step.

153. The process of claim 152, wherein the calcination is at a temperature of at least 325°C for the catalyst precursor to have the formula $(\text{X})_b(\text{Mo})_c(\text{W})_d\text{O}_z$; wherein X is Ni or 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 $z = [2b + 6(c + d)]/2$.

154. The process of any of claims 137-138, further comprising drying the catalyst precursor at a temperature of 200°C or less before the sulfidation step, wherein the catalyst precursor has the formula $\text{A}_v(\text{M}^{\text{P}})(\text{OH})_x(\text{L})^n_{y/z}(\text{M}^{\text{VIB}}\text{O}_4)$, wherein

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

M^{P} is selected from the group of Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, P is oxidation state with M^{P} having an oxidation state of either +2 or +4 depending on the selection of M^{P} ,

L is at least a ligating agent L having an charge $n \leq 0$;

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

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

$v - 2 + P * z - x * z - n * y * z = 0$; and

$0 < y \leq -P/n$; $0 < x \leq P$; $0 < v \leq 2$; $0 < z$.

155. In a process for forming a bulk hydroprocessing catalyst, the process comprising: co-precipitating at reaction conditions at least one of a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor; isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10

mole % of the metal precursor feeds; and sulfiding the catalyst precursor forming the bulk catalyst; the improvement comprising:

supplying the supernatant to a reactor vessel having a plurality of electrodes having a positive or a negative charge provided by a power supply;

5 reacting the electrodes with at least one of the metal residuals, forming a slurry containing insoluble metal compounds;

recovering the insoluble metal compounds, forming a first effluent stream containing less than 50 mole % of at least one of the Promoter metal residual and a Group VIB metal residual; and

10 treating the first effluent stream to recover at least 80 mol % of the metal ions to form at least a metal precursor feed; and

recycling the at least a metal precursor feed to the co-precipitating step.

156. The process of claim 155, wherein
15 the Promoter metal residual comprises at least a Ni compound and the Group VIB metal residual comprises W and Mo compounds.

157. The process of claim 156, wherein the electrodes comprise aluminium and the first effluent stream comprises less than 50 ppm Ni.

20 158. The process of claim 155, wherein treating the first effluent stream comprises adding to the first effluent stream a mineral acid for a pH of less than 3 to precipitate the Group VIB metal residual as metal complexes comprising molybdate, tungstate, and mixtures thereof.

25 159. The process of claim 158, further comprising treating the metal complexes with ammonium hydroxide to recover a slurry containing ammonium heptamolybdate, ammonium heptatungstate, or mixtures thereof.

30 160. The process of claim 159, further comprising isolating and recovering ammonium heptamolybdate, ammonium heptatungstate, or mixtures thereof as metal precursor feed for the co-precipitating step, forming a second effluent stream.

161. The process of claim 160, further comprising adding at least a calcium compound to the second effluent stream under mixing conditions forming a slurry containing at least a calcium salt, wherein the molar ratio of added calcium to Group VIB metal is 2/1 to 50/1.

- 5 162. The process of claim 161, wherein the calcium salt comprises at least one of CaMoO_4 and CaWO_4 .

163. The process of claim 162, further comprising isolating and recovering the calcium salt, forming a third effluent stream containing less than 50 ppm metals.

CLAIMS

1. A process for forming a hydroprocessing catalyst composition with minimal amount of metals to waste treatment, the method comprises:

co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor, wherein the reaction conditions comprise a temperature between 25-350° C. and at a pressure between 0 to 3000 psig and a pH of 0-12;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in a total amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least a base or an acid for a sufficient amount of time to precipitate at least 50 mole % of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a pre-selected pH;

isolating the precipitate to recover a first effluent containing less than 50 mole % of metal ions in at least one of the metal residuals in the supernatant;

contacting the first effluent with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent to be bound onto the resin, forming a second effluent containing less than 1000 ppm of metal ions of at least one of the metal residuals;

eluting the resin to produce an eluate containing the metal ions previously bound onto the resin;

treating the second effluent stream or the eluate to recover at least 80 mol % of the metal ions in the second effluent stream to form at least a metal precursor feed;

recycling the at least a metal precursor feed formed by treating the second effluent stream or the eluate to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst;

wherein an effluent stream from the process to waste treatment contains less than 50 ppm metal ions.

2. The process of claim 1, wherein the chelated ion exchange resin contains an amine functionality group.

3. The process of claim 1, wherein the chelated ion exchange resin has at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine.
4. The process of claim 1, wherein the supernatant is mixed with at least an acid selected from the group of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, acetic acid, oxalic acid, nitric acid, and mixtures thereof.
5. The process of claim 4, wherein the acid is nitric acid and the precipitation is carried out at a pH of less than 3.
6. The process of claim 5, wherein the at least one of a Group VIB metal precursor feed comprises Mo and W compounds, the Promoter metal residual comprises Ni, and the first effluent comprises less than 2000 ppm each of Mo, W, and Ni.
7. The process of claim 6, wherein the first effluent stream is brought into contact with a chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine, for the second effluent to have less than 50 ppm each of Mo and W.
8. The process of claim 7, wherein the second effluent is mixed with at least a base selected from the group of ammonium chloride, ammonium citrate, ammonium lactate, potassium hydroxide, potassium formate, sodium hydroxide, sodium acetate, ammonium hydroxide and mixtures thereof, to adjust its pH to a pre-selected basic pH.
9. The process of claim 8, wherein the second effluent at a pre-selected basic pH is brought into contact with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of the Ni in the second effluent to be exchanged and bound onto the resin, forming a third effluent containing less than 10 ppm Ni.
10. The process of claim 1, further comprising drying the catalyst precursors at a temperature of at least 150° C. before the sulfidation step.

11. The process of claim 10, wherein the catalyst precursor is dried at a temperature of at least 300° C. before the sulfidation step.

12. The process of claim 10, wherein the catalyst precursor is dried at a temperature of at least 325° C. for the catalyst precursor to have the formula $(X)_b(Mo)_c(W)_dO_z$; wherein X is Ni or 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 $z=[2b+6(c+d)]/2$.

13. The process of claim 10, wherein the catalyst precursor is dried at a temperature of at most 200° C. for the catalyst precursor to have the formula $A_v[(M^P)(OH)_x(L)^n]_y(M^{VIB}O_4)_z$, wherein

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

M^P is selected from the group of Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, P is oxidation state with M^P having an oxidation state of either +2 or +4 depending on the selection of M^P ,

L is at least a ligating agent L having an charge $n \leq 0$;

M^{VIB} is 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;

$v-2+(P \cdot z)-(x \cdot z)+(n \cdot y \cdot z)=0$; and

$0 < y \leq -P/n$; $0 < x \leq P$; $0 < v \leq 2$; $0 < z$.

14. The process of claim 1, wherein the sulfiding of the catalyst precursor forming the bulk catalyst is either before or after loading the catalyst precursor into a hydroprocessing reactor.

15. A process for forming a hydroprocessing catalyst composition, the method comprises: co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor, wherein the reaction conditions comprise a temperature between 25-350° C. and at a pressure between 0 to 3000 psig and a pH of 0-12;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least one of a base, an acid, a sulfide-containing compound, and combinations thereof;

contacting the supernatant with a chelated ion exchange resin for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent containing less than 1000 ppm of at least one of the metal residuals;

eluting the resin to produce an eluate stream containing the metal ions previously bound onto the resin;

treating the first effluent stream or the eluate stream to recover at least 80 mol % of the metal ions in the stream to form at least a metal precursor feed;

recycling the at least a metal precursor feed formed by treating the first effluent stream or the eluate to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst.

16. The process of claim 15, wherein the supernatant is mixed with at least an acid selected from the group of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, acetic acid, oxalic acid, nitric acid, and mixtures thereof to adjust its pH to a pre-selected acidic pH.

17. The process of claim 15, wherein the supernatant is brought into contact with a chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine.

18. The process claim 17, wherein the chelated ion exchange resin functions as an anion exchange resin for at least 50 mole % of at least a Group VIB metal residual in the supernatant to be exchanged and bound onto the resin, forming a first effluent containing less than 1000 ppm of Group VIB metals.

19. The process claim 18, wherein the first effluent is brought into contact with at least a base selected from the group of ammonium chloride, ammonium citrate, ammonium lactate, potassium hydroxide, potassium formate, sodium hydroxide, sodium acetate, ammonium hydroxide and mixtures thereof, to adjust its pH to a pre-selected basic pH.

20. The process of claim 19, wherein the first effluent at a pre-selected basic pH is brought into contact with a chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine.

21. The process of claim 20, wherein the chelated ion exchange resin functions as an cation exchange resin for at least 50 mole % of at least a Promoter precursor in the first effluent to be exchanged and bound onto the resin, forming a first effluent containing less than 50 ppm of Promoter metals.

22. A process for forming a hydroprocessing catalyst composition, the method comprises:
co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor, wherein the reaction conditions comprise a temperature between 25-350° C. and at a pressure between 0 to 3000 psig and a pH of 0-12;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;

mixing the supernatant with at least one of an acid, a sulfide-containing compound, and combinations thereof for a sufficient amount of time to precipitate at least a portion of metal ions in at least one of the metal residuals, wherein the precipitation is carried out at a first pre-selected pH;

isolating the precipitate to recover a first effluent stream containing less than 50 mole % of metal ions in at least one of the metal residuals in the supernatant;

contacting the first effluent stream with a first chelated ion exchange resin at a second pre-selected pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent stream to be bound onto the resin, forming a second effluent stream containing less than 1000 ppm of metal ions in at least one of the metal residuals;

contacting the second effluent stream with a second chelated ion exchange resin at a third pre-selected pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the first effluent stream to be bound onto the resin, forming

a third effluent stream containing less than 100 ppm of metal ions in at least one of the metal residuals.

23. The method of claim 22, further comprising adding an acid to the first effluent stream for the first effluent to have a second pre-selected pH prior to contacting the first effluent stream with the first chelated ion exchange resin at the second pre-selected pH.

24. The method of claim 22, further comprising adding a base to the second effluent stream for the second effluent to have a third pre-selected pH prior to contacting the second effluent stream with the second chelated ion exchange resin at the third pre-selected pH.

25. The method of claim 22, wherein the first chelated ion exchange resin and the second chelated ion exchange resin are of the same type.

26. The method of claim 22, wherein the second pre-selected pH is acidic for the first chelated ion exchange resin to function as an anion exchange.

27. The method of claim 26, wherein the second pre-selected pH is 1-2.

28. The method of claim 22, wherein the third pre-selected pH is neutral to basic for the second chelated ion exchange resin to function as a cation exchange.

29. The method of claim 28, wherein the third pre-selected pH is 6-8.

30. A process for forming a hydroprocessing catalyst composition, the method comprises:
co-precipitating at reaction conditions at least a Group VIB metal precursor feed and at least a Promoter metal precursor feed selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof, to form a mixture comprising a catalyst precursor, wherein the reaction conditions comprise a temperature between 25-350° C. and at a pressure between 0 to 3000 psig and a pH of 0-12;

isolating the catalyst precursor from the mixture, forming a supernatant containing at least a Promoter metal residual and at least a Group VIB metal residual in an amount of at least 10 mole % of the metal precursor feeds;

contacting the supernatant with a chelated ion exchange resin at a pre-selected pH for a sufficient amount of time for at least 50 mole % of metal ions in at least one of the metal residuals in the supernatant to be bound onto the resin, forming a first effluent containing less than 1000 ppm of metal ions in at least one of the metal residuals;

eluting the resin to produce an eluate stream containing the metal ions previously bound onto the resin;

treating the first effluent stream or the eluate stream to recover at least 80 mol % of the metal ions in the stream to form at least a metal precursor feed;

recycling the at least a metal precursor feed formed by treating the effluent stream or the eluate stream to the co-precipitating step; and

sulfiding the catalyst precursor forming the bulk catalyst.

31. The process of claim 30, wherein the supernatant is mixed with at least a base selected from the group of ammonium chloride, ammonium citrate, ammonium lactate, potassium hydroxide, potassium formate, sodium hydroxide, sodium acetate, ammonium hydroxide and mixtures thereof, to adjust its pH to the pre-selected pH.

32. The process claim 30, wherein the supernatant is mixed with at least an acid selected from the group of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, acetic acid, nitric acid, and mixtures thereof to adjust its pH to the pre-selected pH.

33. The process of claim 30, wherein the supernatant is brought into contact with a chelated ion exchange resin having at least one substituent selected from hydroxy, ether, amine, quaternary amine, a divalent sulfur substituent, amine oxide and hydroxy amine.

34. The process claim 30, wherein the chelated ion exchange resin functions as a cation exchange resin for at least 50 mole % of metal ions in at least a Promoter metal residual in the supernatant to be exchanged and bound onto the resin, forming a first effluent stream containing less than 1000 ppm of Promoter metals.

35. The process of claim 30, wherein the chelated ion exchange resin functions as an anion exchange resin for at least 50 mole % of metal ions in at least a Group VIB metal residual in the supernatant to be exchanged and bound onto the resin, forming a first effluent stream containing less than 1000 ppm of Group VIB metals.