In another example, U.S. Patent No. 6,559,092 to Dufresne *et al.* describes impregnating a high boiling (*e.g.*, 150 °C to 500 °C) liquid carbon-containing compound (*e.g.*, gas oil) in the pores of a hydrotreating catalyst, carbonizing the carbon-containing compound and then sulfurizing the catalyst. In yet another example, U.S. Patent No. 9,272,276 to Robinson *et al.* describes a soft coking process that provides a layer of coke to be created on the catalyst surface during or along with *in situ* sulfiding using a liquid hydrocarbon source and then introducing cracked hydrocarbon feeds to the reactor.

[0005] Despite the foregoing, the above-mentioned methods require several steps that add processing time, complications, and costly delays when introducing a cracked feedstock to a catalyst bed.

SUMMARY

[0006] A discovery has been made that provides a solution to at least some of the problems associated with the coke and gum formation on hydroconversion catalysts during startup with cracked feedstocks. The solution is premised on methods to combine (*e.g.*, blend) an inactive hydroconversion catalyst with a low melting hydrocarbon solid under conditions that allows the hydrocarbon solid to melt and penetrate the pores of the catalyst. Thus, forming a "coating" or carbonaceous layer on the interior surface of the pores. The inactive hydroconversion catalyst can be an unused catalyst with the catalytic metals being in their metal oxide form that has not been subjected to a sulfiding treatment, or a used catalyst that has been regenerated. The pores of the catalyst can be coated by heating a mixture of the hydrocarbon solid and catalyst and/or heating the catalyst prior to contact with the hydrocarbon solid. The pore-coated catalyst can then be subjected to conditions suitable to sulfurize the active metals in the catalyst and carbonize the hydrocarbon containing material in the pores of the sulfided catalyst to obtain a treated hydroconversion catalyst (*e.g.*, a pre-sulfurized and pre-carbonized catalyst). The method can be performed *ex-situ* of a hydroconversion unit or *in situ* in the hydroconversion unit. In addition, the use of a high melting hydrocarbon with an enhanced ability to form a carbonaceous layer, allows for more efficient use of the hydrocarbon.

[0006a] In one aspect, the present disclosure refers to a method of treating a hydroconversion catalyst, the method comprising:

(a) combining an inactive hydroconversion catalyst with a solid hydrocarbon containing material having a melting point of 50 °C or greater; and

(b) sulfiding the inactive hydroconversion catalyst by contacting the unsulfided hydroconversion catalyst/solid hydrocarbon containing material mixture with a gaseous stream comprising hydrogen (H_2) and a sulfur-containing compound at a temperature sufficient to sulfide the catalyst and carbonize at least a portion of the hydrocarbon containing material on the sulfided catalyst to obtain a treated sulfided hydroconversion catalyst.

[0007] In one example of the present disclosure, methods for treating a hydroconversion catalyst are described. A method can include (a) mixing an inactive (*e.g.*, unsulfided) hydroconversion catalyst with a solid hydrocarbon containing material having a melting point greater than 50 °C; and (b) contacting the inactive hydroconversion catalyst/solid hydrocarbon

containing material mixture with a gaseous stream comprising hydrogen (H_2) and a sulfur-containing compound at a temperature sufficient to sulfide and activate the catalyst and carbonize at least a portion of the hydrocarbon containing material on the sulfided catalyst to obtain a carbonized sulfided hydroconversion catalyst.

[0008] Mixing step (a) can include contacting the catalyst with at least 1 wt. %, preferably 5 wt. % to 25 wt. %, of the solid hydrocarbon containing material based on the total weight of the catalyst and the material. Non-limiting examples of solid hydrocarbon containing material can include a paraffin wax, a microcrystalline wax, a synthetic wax, an animal wax, a plant wax, or blends thereof. In some examples, the catalyst in step (a) is at a temperature lower than the melting point of the solid hydrocarbon containing material at the time the catalyst is contacted with the solid hydrocarbon containing material and sulfiding conditions are sufficient to melt the hydrocarbon containing material and coat the catalyst. This mixture can be heated to a temperature sufficient to melt the hydrocarbon containing material and coat the inactive catalyst. In other examples, the catalyst in step (a) is at a temperature higher than the melting point of the solid hydrocarbon containing material at the time the catalyst is contacted with the solid hydrocarbon containing material (*e.g.*, the catalyst is preheated). Mixing of the hot inactive hydroconversion catalyst with the solid hydrocarbon containing material can penetrate the pores of the inactive hydroconversion catalyst. In step (a), the temperature difference between the catalyst and the melting point of the solid hydrocarbon containing material can be 100 °C or less, preferably 10 °C to 90 °C, or more preferably 30 °C to 75 °C. The melting point of the solid hydrocarbon containing material can be 50 °C to 120 °C, preferably 80 °C to 110 °C. In some examples, a paraffin wax having a melting point of 50 °C to 70 °C, or about 60.5 °C can be used as the solid hydrocarbon containing material. In other examples, a paraffin wax having a melting point of 90 °C to 100 °C, or about 95 °C can be used as the solid hydrocarbon containing material. Temperatures sufficient to sulfide the catalyst and carbonize at least a portion of the hydrocarbon containing material on the catalyst can range from 175 °C to 500 °C. In some examples, the pressure is at or below the sulfiding pressure. Sulfiding pressures can range from 90 kPa to 50,000 kPa. In some examples, step (a) can be performed at a pressure of 90 kPa to 200 kPa and/or sulfiding step (b) can be performed at a pressure of 90 kPa to 150 kPa. In step (b), the gaseous sulfur-containing compound can be hydrogen sulfide gas (H_2S). The gaseous stream in step (b) can include 1 % to 10 % by volume of the sulfur containing compound, at least 2 % by volume of H_2, and the remainder being inert gas (*e.g.*, argon, helium, carbon dioxide, nitrogen or the like).

In some instances, inert gas is not used. The produced pre-treated hydroconversion catalyst can include 2 wt. % to 12 wt. % carbon resulting from the carbonization (*e.g.*, coking) process, preferably 4 wt. % to 10 wt. % carbon, and/or 2 wt. % to 25 wt. % sulfur (S). The hydroconversion catalyst can include at least one catalytically active transition metal. The catalytic metal can be supported on a metal oxide support (*e.g.*, alumina (Al_2O_3), titania (TiO_2), or silica (SiO_2)), or blends thereof either in amorphous or crystalline state.

[0009] The following includes definitions of various terms and phrases used throughout this specification.

[0010] The term "cracked feedstock" refers to the feedstock obtained from crude oil that has been subjected to a chemical process to reduce ("crack") the molecular weight. Examples of cracking processes include thermal cracking and catalytic cracking.

[0011] The term "inactive" is defined as providing less than 1 % conversion in a hydroconversion reaction.

[0012] The terms "about" or "approximately" are defined as being close to as understood by one of ordinary skill in the art. In one non-limiting example, the terms are defined to be within 10%, preferably within 5%, more preferably within 1%, and most preferably within 0.5%.

[0013] The terms "wt.%", "vol.%", or "mol.%" refers to a weight percentage of a component, a volume percentage of a component, or molar percentage of a component, respectively, based on the total weight, the total volume of material, or total moles, that includes the component. In a non-limiting example, 10 grams of component in 100 grams of the material is 10 wt.% of component.

[0014] The term "substantially" and its variations are defined to include ranges within 10%, within 5%, within 1%, or within 0.5%.

[0015] The terms "inhibiting" or "reducing" or "preventing" or "avoiding" or any variation of these terms, when used in the claims and/or the specification includes any measurable decrease or complete inhibition to achieve a desired result.

[0016] The term "effective," as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0017] The use of the words “a” or “an” when used in conjunction with any of the terms “comprising,” “including,” “containing,” or “having” in the claims, or the specification, may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.”

[0018] The words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “includes” and “include”) or “containing” (and any form of containing, such as “contains” and “contain”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0019] The methods of the present disclosure can “comprise,” “consist essentially of,” or “consist of” particular ingredients, components, compositions, etc. disclosed throughout the specification. With respect to the transitional phase “consisting essentially of,” in one non-limiting example, a basic and novel characteristic of the methods of the present disclosure are their abilities to pre-treat a hydroconversion catalyst with sulfur and carbon.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Advantages of the present invention may become apparent to those skilled in the art with the benefit of the following detailed description and upon reference to the accompanying drawings.

[0021] **FIG. 1** is a schematic a method of the present invention to pre-treat a hydroconversion catalyst.

[0022] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings. The drawings may not be to scale.

DETAILED DESCRIPTION OF THE INVENTION

[0023] A discovery has been made that provides a possible solution to the premature deactivation of hydroconversion catalysts in cases when cracked feedstocks are introduced earlier than the recommended seventy-two hour “seasoning” period customarily used by refineries. The solution is premised on providing a hydrocarbon containing material to the pores of an inactive hydroconversion catalyst prior to sulfiding the catalyst and subsequent carbonization of the catalyst. This can be performed by combining or blending a solid

CLAIMS

1. A method of treating a hydroconversion catalyst, the method comprising:

   (a) combining an inactive hydroconversion catalyst with a solid hydrocarbon containing material having a melting point of 50 °C or greater; and

   (b) sulfiding the inactive hydroconversion catalyst by contacting the unsulfided hydroconversion catalyst/solid hydrocarbon containing material mixture with a gaseous stream comprising hydrogen (H_2) and a sulfur-containing compound at a temperature sufficient to sulfide the catalyst and carbonize at least a portion of the hydrocarbon containing material on the sulfided catalyst to obtain a treated sulfided hydroconversion catalyst.

2. The method of claim 1, wherein the catalyst in step (a) is at a temperature lower than the melting point of the solid hydrocarbon containing material at the time the catalyst is contacted with the solid hydrocarbon containing material.

3. The method of claim 2, further comprising heating the mixture to a temperature sufficient to melt the hydrocarbon containing material.

4. The method of claim 1, wherein the catalyst in step (a) is at a temperature greater than the melting point of the solid hydrocarbon containing material at the time the catalyst is contacted with the solid hydrocarbon containing material.

5. The method of any one of claims 2 to 4, wherein the temperature difference between the catalyst and the melting point of the solid hydrocarbon containing material is 120 °C or less, preferably 10 °C to 90 °C, or more preferably 30 °C to 75 °C.

6. The method of any one of claims 1 to 5, wherein the melting point of the solid hydrocarbon containing material is 50 °C to 150 °C, preferably 50 °C to 120 °C.

7. The method of any one of claims 2 to 6, wherein the melted hydrocarbon containing material coats surface of the pores of the unsulfided hydroconversion catalyst.

8. The method of any one of claims 1 to 7, wherein the solid hydrocarbon containing material is a paraffin wax, a microcrystalline wax, a synthetic wax, an animal wax, a plant wax or blends thereof.

9. The method of claim 8, wherein the paraffin wax has a melting point of 50 °C to 70 °C, or about 60.5 °C.

10. The method of claim 8, wherein the paraffin wax has a melting point of 90 °C to 120 °C, or about 95 °C.

11. The method of any one of claims 1 to 10, wherein mixing step (a) comprises contacting the catalyst with at least 1 wt. %, preferably 5 wt. % to 25 wt. %, of the solid hydrocarbon containing material based on the total weight of the catalyst and the material.

12. The method of any one of claims 1 to 11, wherein the temperature sufficient to sulfide the catalyst and carbonize at least a portion of the hydrocarbon containing material on the catalyst is 175 °C to 500 °C.

13. The method of any one of claims 1 to 12, wherein the gaseous sulfur-containing compound is hydrogen sulfide gas (H_2S).

14. The method of any one of claims 1 to 13, wherein the gaseous stream comprises 1 % to 10 % by volume of the sulfur containing compound, at least 0.5 % by volume of H_2.

15. The method of any one of claims 1 to 14, wherein the produced treated sulfided hydroconversion catalyst comprises 2 wt. % to 15 wt. % carbon, preferably 4 wt. % to 7 wt. % carbon produced from carbonization.

16. The method of any one of claims 1 to 15, wherein the produced treated sulfided hydroconversion catalyst comprises 2 wt. % to 25 wt. % sulfur.

17. The method of any one of claims 1 to 16, wherein the catalyst comprises at least one catalytically active transition metal or oxide thereof.

18. The method of claim 17, wherein the catalytic metal is supported on a metal oxide support, preferably alumina (Al_2O_3), titania (TiO_2), or silica (SiO_2).

19. The method of any one of claims 1 to 18, wherein step (a) and step (b) are performed *ex-situ* of a hydroconversion processing unit.

20. The method of any one of claims 1 to 13 and 15 to 19, wherein step (a) and step (b) are performed *in-situ* in a hydroconversion processing unit.