

PROCESS FOR REJUVENATING HYDROTREATING CATALYST

Technical field

[0001] The present invention generally relates to a process for rejuvenating a hydrotreating catalyst, the resulting catalyst obtained through this process and its use in hydrotreating process.

Background Art

[0002] The hydrocarbon feedstocks, the raw materials used in petroleum refining industrial industry, need to be refined before they can be used in numerous products and processes. A large part of the hydrocarbon feedstocks are submitted to a so called hydrotreating process. The purpose of hydrotreating is to reduce the amounts of impurities in the hydrocarbon feedstocks.

[0003] In particular, hydrotreating aims the removal of sulfur and nitrogen compounds.

[0004] The hydrocarbon feedstocks often contain sulfur and nitrogen compounds. These compounds are responsible of the release of sulfur oxides and nitrogen oxides in the atmosphere when the hydrocarbon products are used as fuel and burnt. These sulfur oxides and nitrogen oxides are considered harmful for the environment. As a consequence, national and international regulators are continuously imposing lower nitrogen and sulfur contents in fuel so as to reduce pollution of the environment by reducing as much as possible the quantities of these compounds when the fuel is burnt. There is thus an increased need to develop more efficient hydrotreating processes.

[0005] The efficiency of hydrotreating process relies in part on the activity of hydrotreating catalysts used. These catalysts allow converting feedstocks into useable materials. Nevertheless, at each use, the activity of the catalysts decreases. The resulting spent catalysts may thus be used in less demanding kinds of hydrotreating processes or have to be at least regenerated.

[0006] However, the regenerated catalysts do not show as high activity as the original catalysts due to the formation of agglomerates of catalyst metals.

[0007] Numerous processes have been developed in order to reactivate the spent hydrotreating catalysts such as for example the so-called rejuvenation process. The rejuvenation aims to restore the original activity of the hydrotreating catalysts or at least an activity superior to the one obtained after a simple regeneration step.

[0008] For example, document WO2005/035691 describes a process for activating a hydrotreating catalyst comprising a group VIB hydrogenation metal oxide and a group VIII hydrogenation metal oxide. This process comprises a step of impregnation with a solution comprising an acid and an organic additive which has a boiling point in the range of 80°C to 500°C and a solubility of at least 5g/L (20°C, atmospheric pressure). After the impregnation step, the catalyst is then dried to maintain at least 50wt% of the additive after drying.

[0009] However, the efficiency of the rejuvenation process may depend on several parameters such as: the catalyst to be treated, the operational conditions of the process or the rejuvenating agent used.

[0010] Thus, there is still a need to develop efficient and easy to implement processes for restoring the activity of the spent hydrotreating catalysts.

Technical problem

[0011] It is an object of the present invention to provide an efficient and easy to implement process for rejuvenating hydrotreating catalysts.

[0012] This object is achieved by a process for rejuvenating hydrotreating catalysts as claimed in claim 1.

General Description of the Invention

[0013] In order to overcome the above-mentioned problem, the present invention provides a process for rejuvenating a hydrotreating catalyst comprising a group VIB hydrogenation metal and/or a group VIII hydrogenation metal, which comprises the steps of:

- a) regenerating the catalyst by contacting said catalyst with an oxygen containing gas at a temperature from about 300°C to 550°C,

- b) impregnating the regenerated carbon-reduced catalyst with an impregnation solution which comprises a mixture of water and a combination of MoO_3 and H_3PO_4 ,
- c) aging the impregnated catalyst and
- d) drying the aged catalyst.

[0014] The implementation of this process leads to a significant improvement of the activity of the catalyst.

[0015] Without being bound by any theory, the improvement of the activity of the catalyst seems to be due to:

- The improvement of the dispersion of MoO_3 on the support surface as observed by electronic microscopy;
- The dissolution of undesirable CoMoO_4 or NiMoO_4 crystalline phases as observed by X-Ray diffraction.

[0016] The impregnation solution comprises a mixture of water and a rejuvenating agent (or recovering agent) which is: a combination of MoO_3 and H_3PO_4 .

[0017] The hydrotreating catalyst to be used to this process may be a non-additive based catalyst or an additive based catalyst. The term “non-additive based catalyst” refers to a catalyst wherein no organic additive has been included therein prior to its use in the hydrotreating process of a hydrocarbon feedstock or prior to a presulfurization treatment performed before the use in the hydrotreating process. The term “additive based catalyst” refers to a catalyst wherein an organic additive has been included therein prior to its use in the hydrotreating process of a hydrocarbon feedstock or prior to a presulfurization treatment performed before its use in the hydrotreating process.

[0018] The initial concentration of carbon of the spent hydrotreating catalyst (namely before being submitted to the process for rejuvenating) may for example be comprised from 5wt% to 25wt% based on the total weight of the hydrotreating catalyst before being submitted to the process for rejuvenating.

[0019] The hydrotreating catalyst comprises a group VIB hydrogenation metal. The group VIB hydrogenation metal may be chosen among chromium,

molybdenum, or tungsten. Preferably, the group VIB hydrogenation metal is molybdenum. The amount of group VIB hydrogenation metal may preferably be between 5wt% and 25wt% and more preferably between 10wt% and 20wt% based on the total weight of the hydrotreating catalyst, the concentration of group VIB hydrogenation metal being expressed as element and not as oxide, for example, when group VIB hydrogenation metal is Mo, the concentration is expressed as wt% of Mo instead of wt% of MoO_3 .

[0020] The hydrotreating catalyst also comprises a group VIII hydrogenation metal. The group VIII hydrogenation metal may be preferably selected in the group consisting of iron, cobalt and nickel. In particular, the group VIII hydrogenation metal is cobalt or nickel, or a combination thereof. Advantageously, the amount of group VIII hydrogenation metal is comprised from 1wt% to 8wt% and more advantageously from 3wt% to 5wt% based on the total weight of the hydrotreating catalyst, the concentration of group VIII hydrogenation metal being expressed as element and not as oxide.

[0021] The hydrotreating catalyst may also comprise additional components such as for example, halogens, boron and/or phosphorus. The hydrotreating catalyst may preferably comprise from 0.5wt% to 1wt% and in a more preferred way is about 0.8wt% of boron based on the total weight of the hydrotreating catalyst, the concentration of boron being expressed as element and not as oxide (expressed as B). According to an embodiment, the hydrotreating catalyst comprises from 0.5 to 8wt% and preferably from 0.8 to 5wt% of phosphorus based on the total weight of the hydrotreating catalyst, the concentration of phosphorus being expressed as element and not as oxide (expressed as P).

[0022] The hydrotreating catalyst may also comprise a carrier, preferably a porous carrier. This carrier may be made of alumina and/or silica and alumina is preferred.

[0023] Preferably, the total pore volume of the support may be in the range of from about 0.2 cc/g to about 2 cc/g. Advantageously, the surface area of the support, measured by the B.E.T. (Brunauer, Emmett and Teller) method, may be in the range of from about 100 to about 400 m^2/g .

[0024] Before being submitted to the process for rejuvenating, the hydrotreating catalyst may be previously treated by stripping (before step a) of the process). This optional step of stripping allows removing the volatile hydrocarbons retained on the spent catalyst. The spent catalyst is contacted with a hot steam or gas, diluted air, natural combustion gas products or nitrogen at a temperature comprised from 150°C and 450°C.

[0025] Step a) of the process according to the present invention refers to the regeneration of the hydrotreating catalyst. The regeneration step is carried out by contacting said catalyst with an oxygen containing gas at a temperature comprises from 300°C to 550°C, preferably between 400°C and 500°C. Preferably, the oxygen-containing gas is for example air and the oxygen concentration between 10 and 21%vol. Advantageously, the regeneration step may be performed until the content of carbon of the catalyst decreases below 0.5wt% based on the total weight of the catalyst. According to an embodiment of the invention, the hydrotreating catalyst after the regeneration step a) may for example comprise a content of carbon inferior or equal to 0.4wt%; inferior or equal to 0.3wt%; inferior or equal to 0.2wt%, or inferior or equal to 0.1wt% based on the total weight of the catalyst. According to an embodiment of the invention, the content of carbon of the hydrotreating catalyst after the regeneration step a) may be for example superior or equal to 0; superior or equal to 0.1wt%; superior or equal to 0.2wt%; superior or equal to 0.3wt%; or superior or equal to 0.4wt% based on the total weight of the catalyst.

[0026] Preferably, the percentage of carbon may be inferior to 0.5wt% after the regeneration step a). The catalyst obtained at the end of the regeneration step shows an activity, which may be for example between 75 to 90% versus fresh. The regeneration step generally takes place in a moving belt or a rotary kiln. At the end of the oxidative regeneration, metals supported on carrier are obtained.

[0027] The regenerated carbon-reduced catalyst is then submitted to an impregnation step. In fact, the catalyst is contacted with an aqueous solution. This impregnation solution comprises water and a combination of MoO_3 and H_3PO_4 .

[0028] The rejuvenating agent (or recovering agent) is the combination of MoO_3 and H_3PO_4 . The impregnation of the carbon-reduced catalyst with this

impregnation solution leads to the rejuvenation of said catalyst. The impregnation of the catalyst is carried out preferably up to the total pores saturation of the catalyst.

[0029] The impregnation solution may also comprise optionally Ni and/or Co.

[0030] According to one embodiment, the concentration of MoO_3 is preferably comprised from 0.10 mol of MoO_3 /mol of hydrogenation metals (based on the regenerated catalyst) to 1.0 mol of MoO_3 /mol of hydrogenation metals (based on the regenerated catalyst) and more preferably is about 0.2 mol of MoO_3 /mol of hydrogenation metals (based on the regenerated catalyst). According to a preferred embodiment, the concentration of H_3PO_4 may be comprised from 0.10 mol of H_3PO_4 /mol of hydrogenation metals (based on the regenerated catalyst) to 1.0 mol of H_3PO_4 /mol of hydrogenation metals (based on the regenerated catalyst). Advantageously, the concentration of H_3PO_4 is about 0.30 mol of H_3PO_4 /mol of hydrogenation metals. The concentrations given are based on the amounts of hydrogenation metals measured on the regenerated catalyst.

[0031] According to an embodiment, the concentration of H_3PO_4 in water is comprised from 5 wt% to 25 wt% and more preferably from 7 wt% to 20 wt%.

[0032] Advantageously, the concentration of MoO_3 in water is comprised from 5 wt% to 25 wt% and more advantageously from 7 wt% to 20 wt%.

[0033] According to a specific embodiment of the invention, the impregnation solution consists of a mixture of water and a combination of MoO_3 and H_3PO_4 , by excluding any other compounds.

[0034] Preferably, the mixture of water and a combination of MoO_3 and H_3PO_4 may comprise:

- Water from 90 to 60 wt % of the mixture,
- MoO_3 from 5 to 20 wt % of the mixture, and
- H_3PO_4 from 5 to 20 wt % of the mixture,

provided that the sum of these three components is 100%.

[0035] According to an embodiment of the invention, the impregnated catalyst may be preferably aged for at least 2 hours, preferably for at least 6 hours, more

preferably for at least 12 hours, most preferably for at least 14 hours and in particular for at least 16 hours. The impregnated catalyst may be preferably aged in step c) for example for at least 24 hours, more preferably for at least 40 hours, and even more preferably for at least 96 hours. The aging step is preferably performed at room temperature. During the aging, an exothermic reaction occurs and the temperature of the catalyst may increase until 50°C or even more. Preferably, the end of the aging step occurs when the undesirable crystalline phases such as CoMoO_4 or NiMoO_4 have disappeared. Those crystalline species can be easily monitored by XRD (X-rays Diffraction). According to an embodiment, the aging time does not exceed 504 hours, preferably does not exceed 336 hours and more preferably does not exceed 168 hours.

[0036] After the aging step, the resulting catalyst is then dried in order to remove at least a part the water, preferably at least 80wt% of water and more preferably at least 85wt% of water. The drying step is preferably performed at a temperature comprised from 80°C to 200°C, preferably from 100°C to 150°C, and more preferably is about 120°C. Generally, the drying step is carried out preferably until a residual loss on ignition below 15wt% based on the catalyst weight is reached. This parameter can be measured. This step may last for example about one hour.

[0037] The process may also comprise an optional step, which consists of sulfidizing the rejuvenated catalyst obtained. The sulfidizing step is performed after the step of drying d). Indeed, before being used in hydrotreating, the catalysts are generally sulfided in order to convert the hydrogenation metals into their sulfides.

[0038] The catalysts obtained through the rejuvenation process, show a better activity than the regenerated catalyst and even in certain cases an activity which is superior to the fresh catalysts (namely catalysts which have never been used).

[0039] An aspect of the present invention also concerns the rejuvenated catalyst obtained through this process for rejuvenating and its use for hydrotreating process. In particular, a process for hydrotreating hydrocarbon feedstocks in which a hydrocarbon feedstock is contacted under hydrotreating conditions with a rejuvenated catalyst obtained through the rejuvenation process according to the present invention.

[0040] All the embodiments previously mentioned may be combined within reason.

Examples

[0041] Example 1: Rejuvenation process with a mixture of MoO_3 and H_3PO_4

[0042] The hydrotreating catalysts, namely non-additive based catalysts: Commercial CoMo catalyst 1 (TK-576), Commercial NiMo catalyst 1 (HR-538) and Commercial CoMo catalyst 2 (DC-2532), have been treated with the rejuvenating process using phosphoric acid (H_3PO_4) in combination with MoO_3 . First, the catalysts have been stripped to remove hydrocarbon, then regenerated between 400 and 450°C under air atmosphere to remove carbon and sulfur to achieve carbon content less than 0.5 wt% for those hydrotreating catalysts. After oxidative regeneration, metals supported on alumina carrier are obtained. The physical and the chemical properties of the regenerated catalysts are as follows:

	Commercial CoMo catalyst 1	Commercial NiMo catalyst 1	Commercial CoMo catalyst 2
Carbon content (wt%)	0.34	0.05	0.16
Sulfur content (wt%)	0.52	0.21	0.34
Surface area (m^2/g)	196	202	199
Water Pore Volume (cc/g)	0.465	0.578	0.567
LOI at 485°C (wt%)	1.81	0.67	1.09
Cobalt content (wt%)	3.55	-	3.10
Molybdenum content (wt%)	14.68	10.84	10.85
Nickel content (wt%)	-	2.28	0.56
Phosphorus content (wt%)	-	2.51	2.16
Boron content (wt%)	0.82	-	-

[0043] The regenerated catalysts have been impregnated with phosphoric acid in association with MoO_3 , in aqueous solution, up to total pores saturation. The concentration of MoO_3 in water, namely the concentration of MoO_3 impregnation solution used to impregnate the regenerated catalyst is: 11.1 MoO_3 wt% for Commercial CoMo catalyst 1; 6.8 MoO_3 wt% for Commercial NiMo catalyst 1 and 7.8 MoO_3 wt% for Commercial CoMo catalyst 2. The concentration of H_3PO_4 in water, namely the concentration of H_3PO_4 in impregnation solution used to impregnate the regenerated catalyst is: 12.5 H_3PO_4 wt% for Commercial CoMo catalyst 1; 7.6 H_3PO_4 wt% for Commercial NiMo catalyst 1 and 8.8 H_3PO_4 wt% for Commercial CoMo catalyst 2. Then, the regenerated-impregnated catalysts have been aged for at least 16 hours at room temperature to obtain an aged-impregnated catalyst. The aged-impregnated catalysts have been dried at 120°C during about 1 hour to obtain rejuvenated catalysts.

[0044] The chemical composition of the rejuvenated hydrotreating catalysts after the regeneration and the impregnation steps is as follows:

	Commercial CoMo catalyst 1		Commercial NiMo catalyst 1		Commercial CoMo catalyst 2	
	Regenerated	Rejuvenated	Regenerated	Rejuvenated	Regenerated	Rejuvenated
Mo (wt%)	14.68	16.90	10.84	13.10	10.85	12.95
Co (wt%)	3.55	3.26	-	-	3.10	2.89
Ni (wt%)	-	-	2.28	2.11	0.56	0.53
P (wt%)	-	1.94	2.51	4.01	2.16	3.96

[0045] The activities of regenerated and rejuvenated Commercial CoMo catalyst 1 have been checked with SRGO+ feedstock using the following operational

conditions: P = 30 bar; LHSV (Liquid Hourly Space Velocity) = 1.5 hr^{-1} ; H_2/Oil = 250 sl/l; WABT (Weighted Average Bed Temperature) = 350°C .

[0046] The activities of regenerated and rejuvenated Commercial NiMo catalyst 1 have been checked with SRGO+ feedstock using the following operational conditions: P = 35 bar; LHSV = 1.3 hr^{-1} ; H_2/Oil = 200 sl/l; WABT = 335 to 355°C .

[0047] The activities of regenerated and rejuvenated Commercial CoMo catalyst 2 have been checked with SRGO+ feedstock using the following operational conditions: P = 41.4 bar; LHSV = 1.5 hr^{-1} ; H_2/Oil = 214 sl/l; WABT = 343°C .

[0048] The composition of SRGO+ feedstock is:

SULFUR	MG/KG	8920
NITROGEN BASIC	MG/KG	26.0
NITROGEN	MG/KG	50
DENSITY AT 25°C	G/ML	
DENSITY AT 15°C	G/ML	0.8388
HYDROGEN	WT%	
MONO-AROMATICS	WT%	15.8
DI-AROMATICS (DAH)	WT%	9.7
TRI+-AROMATICS (T+AH)	WT%	0.5
BROMINE NUMBER	G/100G	1.1

[0049] The hydrodesulfurization relative volume activity has been measured for every rejuvenated catalyst. The following results have been obtained.

	Commercial CoMo catalyst 1	Commercial NiMo catalyst 1	Commercial CoMo catalyst 2
Fresh	100%	100%	100%
Regenerated	85%	85%	91%
Example 1 (according to the invention)	95%	98%	103%

[0050] The activity results are expressed as percentage of fresh catalyst. These results show that the rejuvenated catalysts are more efficient than the regenerated ones and even more efficient than the fresh ones in term of hydrodesulfurization (HDS) activity, in particular for the rejuvenated Commercial CoMo catalyst 2 for which the activity is superior to 100%.

[0051] Example 2: Additional results

[0052] Catalyst DN-3100 has been rejuvenated with the process according to the present invention. The hydrodesulfurization relative volume activity (HDS-RVA) has been measured for the rejuvenated catalyst prepared.

[0053] The composition of the regenerated hydrotreating catalyst is:

Catalyst	Carbon content (wt%)	Molybdenum content (wt%)	Cobalt content (wt%)	Nickel content (wt%)	Phosphorus content (wt%)
Example 2 (DN-3100)	0.05	12.47	-	3.10	3.13

[0054] The hydrotreating catalyst has been submitted to the impregnation step according to the following conditions:

Example	Concentration of the impregnating solution (wt%)	Concentration (mol/mol of hydrogenation metals) of	Drying temperature (°C)	Aging time (hours)
2 (catalyst DN-3100)	- MoO_3 = 9.9 - H_3PO_4 = 11.2	- 0.2 mol MoO_3 /mol of hydrogenation metals - 0.34 mol H_3PO_4 /mol of hydrogenation metals	120	>16

[0055] The activity of regenerated and rejuvenated DN-3100 catalyst has been checked with LGO (Light Gas Oil) feedstock using the following operational conditions: P = 41.4 bar; LHSV = 1.0 hr⁻¹; H₂/Oil = 214 sl/l; WABT = 354.5°C.

[0056] The composition of LGO feedstock is:

SULFUR	MG/KG	11000
NITROGEN BASIC	MG/KG	44.0
NITROGEN	MG/KG	120
DENSITY AT 25°C	G/ML	
DENSITY AT 15°C	G/ML	0.8534
HYDROGEN	WT%	
MONO-AROMATICS	WT%	17.1
DI-AROMATICS (DAH)	WT%	11.5
TRI+-AROMATICS (T+AH)	WT%	1.0
POLYCYCLIC AROMATIC	WT%	12.5
TOTAL AROMATICS	WT%	29.6
BROMINE NUMBER	G/100G	1.0

[0057] The result obtained is:

Example	HDS-RVA (regenerated catalyst) %	HDS-RVA (rejuvenated catalyst) %
2 (catalyst DN-3100)	79	112

[0058] The rejuvenated catalyst shows excellent percentage of HDS-RVA. This percentage is even superior to 100 which means that the activity of the rejuvenated catalyst is superior than the fresh catalyst.

[0059] These results prove that the rejuvenating process according to the present invention allows recovering catalyst's activity superior to the regenerated catalysts and even superior to the fresh catalysts. Thus, the rejuvenated catalyst has recovered a catalytic activity superior to the fresh catalyst.

Claims

1. A process for rejuvenating a hydrotreating catalyst comprising a group VIB hydrogenation metal and/or a group VIII hydrogenation metal, which comprises the steps of:
 - a) regenerating the catalyst by contacting said catalyst with an oxygen containing gas at a temperature from about 300°C to 550°C,
 - b) impregnating the regenerated carbon-reduced catalyst with an impregnation solution comprising a mixture water and a combination of MoO_3 and H_3PO_4 ,
 - c) aging the impregnated catalyst and
 - d) drying the aged catalyst.
2. The process according to claim 1, wherein the temperature of the drying step d) is comprised from 80°C to 200°C and preferably is about 120°C.
3. The process according to any of the preceding claims, wherein the content of carbon at the end of the regeneration step a) is inferior to 0.5wt% based on the total weight of the catalyst.
4. The process according to any of the preceding claims, wherein the concentration of MoO_3 is comprised from 0.10 mol of MoO_3 /mol of hydrogenation metals to 1.0 mol of MoO_3 /mol of hydrogenation metals.
5. The process according to any of the preceding claims, wherein the concentration of H_3PO_4 is comprised from 0.10 mol of H_3PO_4 /mol of hydrogenation metals to 1.0 mol of H_3PO_4 /mol of hydrogenation metals.
6. The process according to any of the preceding claims, wherein the concentration of MoO_3 in the impregnation solution is comprised from 5wt% to 25wt%.
7. The process according to any of the preceding claims, wherein the concentration of H_3PO_4 in the impregnation solution is comprised from 5wt% to 25wt%.
8. The process according to any of the preceding claims, wherein the impregnation solution comprises Co and/or Ni.

9. The process according to any of the preceding claims, wherein the impregnation solution consists of a mixture of water and a combination of MoO_3 and H_3PO_4 , by excluding any other compounds.
10. The process according to any of the preceding claims, wherein the hydrotreating catalyst is a non-additive based catalyst or an additive based catalyst.
11. The process according to any of the preceding claims, wherein the hydrotreating catalyst, before being submitted to the process, comprises: from 10 to 20wt% of group VIB hydrogenation metal and/or from 3 to 5wt% group VIII hydrogenation metal, the concentration of group VIB hydrogenation metal and the concentration of group VIII hydrogenation metal being expressed as element.
12. The process according to any of the preceding claims, wherein the group VIB hydrogenation metal is molybdenum.
13. The process according to any of the preceding claims, wherein the group VIII hydrogenation metal is cobalt, nickel or a mixture thereof.
14. The process according to any of the preceding claims, wherein the hydrotreating catalyst comprises halogens, phosphorus, boron or any mixture thereof.
15. The process according to any of the preceding claims, wherein the hydrotreating catalyst comprises a porous carrier which preferably comprises alumina.
16. The process according to any of the preceding claims, wherein it comprises a stripping step prior to step a).
17. The process according to any of the preceding claims, wherein it comprises a sulfidation step after step d).
18. The process according to any of the preceding claims, wherein the aging time of the impregnated catalyst lasts in step c) for at least 2 hours, preferably for at least 6 hours, more preferably for at least 12 hours, most preferably for at least 14 hours and in particular for at least 16 hours.
19. The process according to any of the preceding claims, wherein the aging time of the impregnated catalyst in step c) does not exceed 504 hours, preferably does not exceed 336 hours and more preferably does not exceed 168 hours.

20. A process for hydrotreating hydrocarbon feedstocks in which a hydrocarbon feedstock is contacted under hydrotreating conditions with a rejuvenated catalyst obtained through the process according to any of the preceding claims.
21. A rejuvenated hydrotreating catalyst obtained through the process for rejuvenating according to any of the claims 1 to 19.