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EUROPEAN PATENT APPLICATION

(21) Application number: 80300777.2

(51) Int. Cl.³: **C 10 G 35/22**

(22) Date of filing: 13.03.80

(43) Date of publication of application:
23.09.81 Bulletin 81/38

(84) Designated Contracting States:
DE FR GB NL

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(54) **Startup method for a hydrocarbon reforming process utilizing a bed containing an iridium component and a platinum group component reforming catalyst having a substantially uniform sulfur distribution throughout the bed.**

(57) A bed of hydrocarbon reforming catalyst comprising an iridium component and at least one other metal component from the platinum group or Group 1B of the Periodic Table on a refractory support is treated to have a uniform sulfur distribution within the range of from 0.3 to 2.0 atoms of sulfur per atom of metal components at the start-up of a hydrocarbon reforming process. The uniform sulfur distribution within the specified range is achieved by contacting a bed of reduced fresh or regenerated catalyst with a sulfiding agent (e.g H₂S) until the sulfur content is 0.3 to 2.0 or more atoms of sulfur per atom of metal components and subsequently contacting the sulfided catalyst with a hydrogen-containing gas at a temperature of 482 to 510 °C until H₂S evolution substantially ceases. The hydrocarbon feed is thereafter passed in contact with the catalyst.

EP 0 036 048 A1

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Ref: US 961374

Startup Method for a Hydrocarbon Reforming Process Utilizing
a Bed Containing an Iridium and a Platinum Group Component
Reforming Catalyst having a Substantially Uniform Sulfur
Distribution throughout the Bed

This invention relates to a startup method for a hydrocarbon reforming process utilizing a bed containing an iridium and a platinum group component reforming catalyst having a substantially uniform sulfur distribution throughout the bed.

Reforming catalysts comprising an iridium component and a platinum group component composited with a suitable refractory support are well known.

U.S. Patent 3,578,582 discloses sulfiding a reduced platinum-rhenium catalyst and subsequently contacting the sulfided catalyst with hydrogen prior to introducing the naphtha feed into contact with the catalyst.

Sulfiding a reduced tri-metallic reforming catalyst to incorporate low levels of sulfur on the catalyst is also known. See, for example, U.S. Patent 3,936,369 wherein the catalyst comprises iridium, germanium, and platinum or palladium and 0.05 to 0.5 weight percent sulfur; U.S. Patent 3,939,060 wherein the catalyst comprises iridium, nickel, platinum or paladium and 0.01 to 1 weight percent sulfur; and U.S. Patent 4,082,651 wherein the catalyst comprises rhodium, rhenium and platinum or palladium and 0.01 to about 1 weight percent sulfur.

Polymetallic cluster catalysts, including bimetallic cluster catalysts, comprising an iridium component and a platinum group metal component are also known. See U.S. Patent 3,953,368.

It has now been found that a startup method for an iridium and platinum group metal-containing reforming catalyst at specified conditions will provide advantages that will become apparent in the ensuing description.

In accordance with the invention there is provided, in a startup method for a reforming process wherein a substantially sulfur-free hydrocarbonaceous feed is contacted under reforming conditions in the presence of hydrogen with a bed of a fresh or regenerated catalyst comprising metal components and a refractory support, said metal components comprising an iridium component and at least one additional metal component selected from ruthenium, rhodium, palladium, osmium, platinum, copper, silver and gold, said fresh or regenerated catalyst having been reduced by contact with a reducing agent, the method comprising the steps of: (a) contacting the reduced catalyst with a sulfiding agent in a sulfiding zone to provide from 0.3 to 2.0 atoms or more of sulfur per atom of said metal components, and subsequently (b) contacting the resulting sulfided catalyst with a hydrogen-containing gas at a temperature in the range of from 900 to 950°F. (482 to 510°C) until gas which has been passed in contact with the catalyst is substantially free of H_2S whereby to produce a catalyst whose composition at all regions of the zone is not outside the range of from 0.3 to 2.0 atoms of sulfur per atom of said metal components, excess sulfur thereby having been removed from catalyst in said sulfiding zone and said remaining sulfur being substantially uniformly distributed throughout said bed prior to contacting said sulfided catalyst with said hydrocarbonaceous feed.

The startup method of the present invention is suitable for use at the beginning of a reforming process utilizing a fresh or a regenerated reforming catalyst comprising an iridium component and at least one additional metal component.

The startup method of the present invention is particularly suited to start up a naphtha hydroforming (reforming) process utilizing a substantially sulfur-free naphtha feed that typically contains about 20 to about 80 volume

1 percent paraffins, 20 to 80 volume percent naphthenes,
2 and about 5 to about 20 percent aromatics, and boiling at
3 atmospheric pressure substantially between about 80 and
4 450°F., preferably between 150 and 375°F. By "substantially
5 sulfur-free" is intended herein that the feed contains
6 less than about 25 wppm sulfur, preferably less than 10
7 wppm sulfur. A suitable feed, as given above, is brought
8 into contact with the pretreated reforming catalyst of the
9 present invention in the presence of hydrogen under conven-
10 tional reforming conditions. The reactions typically take
11 place in the vapor phase at a temperature ranging from
12 about 650 to about 1000°F., preferably from about 750 to
13 about 980°F. Reaction zone pressures may vary from about 1
14 to about 50 atmospheres, preferably from about 5 to about
15 25 atmospheres.

16 A naphtha feed stream is generally passed over the
17 catalyst at space velocities ranging from 0.5 to 20 parts
18 by weight of naphtha per hour per part by weight of catalyst
19 (W/Hr/W), preferably from about 1 to 10 W/Hr/W. The hydro-
20 gen to hydrocarbon mole ratio within the reaction zone is
21 maintained between about 0.5 and 20, preferably between 1
22 and 10. During the reforming process, the hydrogen employed
23 can be in admixture with light gaseous hydrocarbons. Since
24 the hydro-forming process produces hydrogen, a recycle
25 stream is employed for admission of hydrogen with the feed.
26 In a typical operation, the catalyst is maintained as a
27 fixed bed within a series of adiabatically operated reactors.
28 Specifically, the product stream from each reactor, except
29 the last, in the reactor series is reheated prior to passage
30 to the following reactor. As an alternate^{iv} to the above-
31 described process sequence, the catalyst may be employed in
32 a moving bed in which the naphtha feed, hydrogen and catalyst
33 are passed in parallel to the reactor, or in a fluidized
34 system wherein the naphtha feed is passed upwardly through a
35 turbulent bed of finely divided catalyst. The catalysts
36 which find use in the method of the present invention com-

1 prise a support and metal components consisting of iridium
2 and at least one additional metal component selected from
3 the group consisting of platinum group metals, copper, sil-
4 ver and gold. Most preferably, the catalytic metal com-
5 ponents consist of iridium and one additional metal com-
6 ponent selected from the group consisting of ruthenium,
7 rhodium, palladium, osmium and platinum. Generally, the
8 iridium component is present in the catalyst in an amount
9 ranging from about 0.01 to 3 weight percent and the addi-
10 tional metal component is present in an amount ranging from
11 about 0.01 to about 3 weight percent, said weights being
12 calculated as if the iridium component and the additional
13 metal component were present in the elemental metallic
14 state, based on the total weight of the dry catalyst. The
15 term "platinum group" is used herein to refer to all the
16 noble metals of Group VIII of the Periodic Table of Elements
17 as well as compounds and mixtures thereof. Platinum is pre-
18 ferred as the platinum group component.

19 The support or carrier component of the catalyst
20 used in the present invention is preferably a porous adsorbent
21 material having a surface area, as determined by the
22 Brunauer-Emmett-Teller (BET) method, of from about 20 to
23 about 800, preferably from about 100 to about 300 square
24 meters per gram. The support material should be substan-
25 tially refractory at temperature and pressure conditions
26 utilized in the reforming process. Typical porous inorganic
27 oxide supports are the naturally occurring aluminosilicates,
28 naturally occurring or synthetically prepared alumina, mag-
29 nesia, silica-alumina, silica-zirconia, silica-alumina-
30 zirconia, silica-alumina-magnesia and crystalline aluminosili-
31 cate zeolites. The preferred catalyst supports are alumina
32 and silica-alumina. The particularly preferred catalytic
33 support is alumina. Any of the forms of alumina suitable as
34 supports for reforming catalysts can be used. The catalyst
35 may be promoted for reforming by the addition of halides,
36 particularly fluorides or chlorides. The halogen in the

1 catalyst may be present in an amount ranging from about
2 0.1 to about 3 weight percent, based on the total weight
3 of the catalyst. The halogen may be incorporated into the
4 catalyst at any suitable stage in the catalyst manufacture,
5 i.e., before, during, or after incorporation of the catalytic
6 metals onto the support material. Halogen may also be in-
7 corporated by contacting the catalyst with a gaseous stream
8 containing the halogens, generally chlorine.

9 A preferred catalyst for use in the present inven-
10 tion is a bimetallic cluster catalyst having clusters of an
11 average size of less than about 50 Angstroms, such as the
12 catalysts described in U.S. Patent 3,953,368. The preferred
13 catalyst comprises metal components and a refractory support.
14 The metal components consist essentially of an iridium com-
15 ponent and at least an additional metal component selected
16 from the group consisting of ruthenium, rhodium, palladium,
17 osmium, platinum, copper, silver and gold. More preferably,
18 the catalyst comprises a refractory support and an iridium
19 component and a platinum component. The iridium component
20 may suitably be present in an amount of about 0.01 to 3
21 weight percent, preferably from 0.1 to 1 weight percent, cal-
22 culated as the metal, based on the total dry catalyst. The
23 platinum component may suitably be present in an amount
24 ranging from about 0.01 to 3 weight percent, preferably 0.1
25 to about 1, more preferably 0.15 to 0.5 weight percent, cal-
26 culated as the metal, based on the total dry catalyst. Addi-
27 tionally, a halogen component may be present in the catalyst,
28 suitably in amounts of about 0.1 to 3 weight percent, based
29 on the total catalyst. In the preparation of the preferred
30 cluster catalyst, as taught in U.S. Patent 3,953,368, fol-
31 lowing the impregnation of the support with the metal com-
32 ponents, the catalyst is dried at temperatures varying from
33 220 to 250°F. The catalyst may simply be dried in air at
34 the above-stated temperature or may be dried by treating the
35 catalyst in a flowing stream of inert gas or hydrogen. The
36 drying step may be followed by an additional calcination step

1 at a temperature of about 500 to 700°F. Care must be taken
2 to avoid contacting the catalyst at temperatures in excess
3 of 700 to 850°F. with air or other gas of high oxygen con-
4 centration. Otherwise, large iridium oxide crystallites
5 will be formed and the desired metallic clusters will not
6 be obtained on reduction. The catalyst is typically reduced
7 at a temperature of 500 to 1000°F. or higher with a hydrogen-
8 containing gas prior to use, for example, for a period of
9 at least 0.1 hours.

10 In accordance with the present invention, the re-
11 duced catalyst is contacted with a sulfiding agent for a time
12 sufficient to provide from about 0.3 to about 2.0 atoms of
13 sulfur per atom of said metal components, preferably from
14 about 0.1 to about 0.5 atoms of sulfur per atom of said metal
15 components, that is, of the iridium plus at least one of
16 said metal components.

17 Contact of the catalyst with the sulfiding agent is
18 suitably conducted at elevated temperatures and pressures,
19 suitably at a temperature ranging from about 75 to about
20 1000°F. and at a pressure ranging from about 20 to about 500
21 psig, with conventional sulfiding agents such as hydrogen
22 sulfide, precursors of hydrogen sulfide, carbon disulfide,
23 mercaptans, as is well known in the art. The sulfiding step
24 is generally conducted in the presence of hydrogen. After
25 the catalyst has been sulfided for a time sufficient to pro-
26 vide the desired low level of sulfur on the catalyst, the
27 sulfided catalyst is contacted with a hydrogen-containing
28 gas at a temperature ranging from about 900 to about 950°F.,
29 preferably at a temperature of at least 925°F. and a pres-
30 sure of about 20 to about 500 psig for a time sufficient to
31 provide uniform distribution of the sulfur throughout the
32 catalyst bed and to remove the excess sulfiding agent from
33 the sulfiding zone, for example, for a period of at least
34 about 0.5 hour, suitably for a time ranging from about 0.5
35 to about 24 hours. The hydrogen utilized may be pure hydro-
36 gen but will generally be a hydrogen stream containing some

1 other gaseous components, for example, the hydrogen-
2 containing effluent gas produced in the reforming process.

3 The resulting catalyst is subsequently contacted
4 with the hydrocarbonaceous feed at reforming conditions.

5 EXAMPLE 1 (Using Prior Art Startup)

6 An experimental reforming run was performed utiliz-
7 ing a platinum-iridium-alumina catalyst comprising 0.3
8 weight percent platinum and 0.3 weight percent iridium. The
9 hydrocarbonaceous feed used was a mixed naphtha which had an
10 API gravity of 54.5 at 60°F., about 46 volume percent paraf-
11 fins, about 43 volume percent naphthenes and the balance
12 being aromatics.

13 The startup procedure used was a prior art procedure.
14 The catalyst was sulfided at 700°F. in a gaseous mixture com-
15 prising hydrogen and hydrogen sulfide. The resulting cata-
16 lyst comprised 0.1 weight percent sulfur, or expressed in
17 terms of atomic ratio, 0.93 atom sulfur per atom of metal,
18 after the treat. The conditions utilized during the experi-
19 mental run were 200 psig. 900°F. average catalyst tempera-
20 ture, a hydrogen-rich gas recycle rate of 6000 SCF/B. The
21 hydrocarbonaceous feed rate was adjusted to obtain a product
22 with a Research Octane number of 100.

23 EXAMPLE 2 (Using Startup of Present Invention)

24 Another experimental run was performed utilizing a
25 platinum-iridium-alumina catalyst comprising about 0.3 weight
26 percent platinum and 0.3 weight percent iridium.

27 The hydrocarbonaceous feed used was a naphtha having
28 the same proportions of constituents and gravity as the feed
29 used in Example 1.

30 The catalyst was pretreated in accordance with the
31 startup procedure of the present invention as follows: The
32 catalyst was sulfided at 700°F. in a gaseous mixture compris-
33 ing hydrogen and hydrogen sulfide. Subsequently, the cata-
34 lyst was heated in a hydrogen stream at 950°F. until there
35 were less than 2 volume ppm of the H_2S in the reactor efflu-
36 ent gas. This treatment left 0.029 wt. % sulfur, or ex-

1 pressed another way, 0.27 sulfur atom per metal atom, on
2 the catalyst.

3 The test conditions were 200 psig, 900°F. average
4 catalyst temperature, a hydrogen-rich gas recycle rate of
5 6000 SCF/B. The hydrocarbonaceous feed rate was adjusted
6 to obtain a product with a Research Octane Number of 100.
7 Results of the comparative experiments of Example 1 and
8 Example 2 are summarized in Table I.

9

10 TABLE I

11 Relative Catalyst Activity

12 <u>Hours on Feed</u>	13 <u>Example 1</u>	14 <u>Example 2</u>
15 200	98	112
16 400	82	100
17 600	75	100

18 As can be seen from Table I, Example 2, which used
19 the startup method of the present invention, resulted in im-
20 proved catalyst activity and activity maintenance.

21 EXAMPLE 3 (Comparative Example)

22 In this test, a platinum-iridium-alumina catalyst
23 comprising about 0.3 wt. % platinum and 0.3 wt. % iridium
24 was sulfided according to a prior art method, in a gaseous
25 mixture comprising hydrogen and hydrogen sulfide at 700°F.
26 Subsequently, the catalyst was removed from the reactor and
27 the sulfur level on the catalyst was measured at various
28 points in the catalyst bed to determine the uniformity of
29 the sulfur distribution. The bed was divided into three
30 equal parts and it was found that the inlet third of the
31 catalyst comprised 0.092 wt. % sulfur, the middle third com-
32 prised 0.054 wt. % sulfur, and the outlet third comprised
33 0.048 wt. % sulfur. Thus, the sulfur was not uniformly dis-
34 tributed and the average sulfur content for the catalyst
35 bed was 0.065 wt. %, or expressed another way, it was 0.6
36 atom sulfur per atom of metal.

37 EXAMPLE 4

38 In this test a platinum-iridium-alumina catalyst
39 comprising about 0.3 wt. % platinum and 0.3 wt. % iridium

1 was sulfided in accordance with the method of the present
2 invention, in a gaseous mixture comprising hydrogen and
3 hydrogen sulfide at about 950°F., then heated in a hydro-
4 gen stream until there were less than 2 vol. ppm of H₂S in
5 the reactor effluent gas. Subsequently, the catalyst was
6 removed from the reactor and the sulfur level on the cata-
7 lyst was measured at various points in the catalyst bed to
8 determine the distribution of the sulfur. The catalyst bed
9 was divided into three equal parts and it was found that
10 the inlet third of the catalyst comprises 0.033 wt. % sulfur,
11 the middle third comprised 0.04 wt. % sulfur and the outlet
12 third comprised 0.037 wt. % sulfur. Thus, the sulfur on
13 the catalyst bed was found to be evenly distributed with
14 the test run of Example 4 which was performed using the
15 startup method of the present invention. Furthermore, the
16 average sulfur for the entire bed was 0.037 wt. % or, ex-
17 pressed another way, it was 0.34 atom of sulfur per metal
18 atom of the catalyst. Moreover, the sulfur content of the
19 catalyst of Example 4 was lower than the sulfur content of
20 the catalyst of Example 3, which was the comparative prior
21 art run.

22 EXAMPLE 5

23 A platinum-iridium-alumina catalyst comprising 0.3
24 wt. % platinum and 0.3 wt. % iridium was sulfided in a
25 gaseous mixture comprising hydrogen and hydrogen sulfide at
26 700°F. for a time sufficient to deposit 0.07 wt. % sulfur on
27 the catalyst. The catalyst was then heated in a hydrogen
28 stream and the hydrogen sulfide concentration in the reactor
29 effluent gas was monitored continuously. There was no de-
30 tectable hydrogen sulfide in the effluent gas until the tem-
31 perature exceeded the temperature of 850°F. and there was no
32 significant detectable hydrogen sulfide in the effluent gas
33 until the temperature reached 900°F. The results of this
34 test are summarized in Table II.

TABLE II

<u>Catalyst Temperature</u>	<u>Vol. PPM H₂S in Effluent Gas</u>
700°F.	0
750°F.	0
800°F.	0
850°F.	0.3
900°F.	1.7
950°F.	4.4

The data of Table II show that a critical temperature range is required to remove the excess sulfur from the catalyst, said range being from about 900°F. to about 950°F.

Conversion of Units

- (1) Temperatures given in °F are converted to °C by subtracting 32 and then dividing by 1.8.
- (2) Pressures given in psig (pounds/in² gauge) are converted to kg/cm² gauge by multiplying by 0.07031.
- (3) Volumes (gas) in Standard Cubic Feet (SCF) are converted to litres by multiplying by 28.32.
- (4) Volumes (liquid) in barrels (B) are converted to litres by multiplying by 159.0.

CLAIMS:

1. A startup method for a reforming process wherein a substantially sulfur-free hydrocarbonaceous feed is contacted under reforming conditions in the presence of hydrogen with a bed of a fresh or regenerated catalyst comprising metal components and a refractory support, said metal components comprising an iridium component and at least one additional metal component selected from ruthenium, rhodium, palladium, osmium, platinum, copper, silver and gold, said fresh or regenerated catalyst having been reduced by contact with a reducing agent, characterized in that it comprises the steps of:

(a) contacting the reduced catalyst with a sulfiding agent in a sulfiding zone to provide more than 0.3 to 2.0 atoms of sulfur per atom of said metal components and, subsequently,

(b) contacting the resulting sulfided catalyst with a hydrogen-containing gas at a temperature in the range of from 900 to 950°F. (482 to 510°C) until gas which has been passed in contact with the catalyst is substantially free of H_2S whereby to produce a catalyst whose composition at all regions of the zone is not outside the range of from 0.3 to 2.0 atoms of sulfur per atom of said metal components, and the ratio of atoms of sulfur to atoms of metal components is substantially uniform in the zone prior to contacting said sulfided catalyst with said hydrocarbonaceous feed.

2. The method of claim 1 characterized in that said reduced catalyst is contacted with said sulfiding agent such as to provide from 0.1 to 0.5 atoms or more of sulfur per atom of said metal components.

3. The method of claim 1 or claim 2 characterized in that said reduced catalyst is contacted with said sulfiding agent in said sulfiding zone of step (a) in the presence of hydrogen.
4. The method of any one of claims 1 to 3 characterized in that said catalyst is contacted with an oxidizing gas at a temperature not greater than about 700°F prior to said reduction step.
5. The method of any one of claims 1 to 4 characterized in that catalyst is contacted with said hydrogen-containing gas for a period of time of at least about 0.5 hour.
6. The method of any one of claims 1 to 5 characterized in that said catalyst is contacted with said reducing agent at a temperature ranging from about 500 to about 700°F for a time sufficient to reduce said metal components substantially to the corresponding elemental metals.
7. The method of any one of claims 1 to 6 characterized in that said catalyst comprises a halogen component.
8. The method of any one of claims 1 to 7 characterized in that said refractory support is an inorganic oxide.
9. The method of any one of claims 1 to 8 characterized in that said metal components are present as clusters having an average size not greater than about 50 Angstroms.
10. The method of any one of claims 1 to 9 characterized in that said catalyst comprises bimetallic clusters consisting essentially of iridium and platinum dispersed on an inorganic oxide support, said clusters having an average size not greater than about 50 Angstroms, said iridium being present in the total catalyst in an amount greater than about 0.1 weight percent and said platinum being present in the total catalyst in an amount ranging from about 0.1 to about 1 weight percent.



European Patent
Office

EUROPEAN SEARCH REPORT

0036048

Application number

EP 80 30 0777

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>US - A - 4 048 058</u> (PETERSEN et al.) * Abstract; claims 22,31; column 3, lines 39-41; column 9, lines 15-25; column 6, lines 10-18 * --	1-8	C 10 G 35/22
	<u>US - A - 4 159 938</u> (LEWIS) * Claims 1,3,5,6,10,12 * --	1,2,3,5-8	
D	<u>US - A - 3 578 582</u> (JACOBSON) * Claims 1-4; column 5, lines 39-54 * --	1-8	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 10 G 35/22 B 01 J 37/20 23/96 23/46
D	<u>US - A - 3 939 060</u> (HAYES) * Claims 1-4, 8-11, 13,14 * --	1-3,5-8	
D	<u>US - A - 3 936 369</u> (HAYES) * Claims 1-8 * --	1-3,5-8	
DA	<u>US - A - 3 953 368</u> (SINFELT) * Abstract * ----	1,9,10	CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<div style="border: 1px solid black; padding: 2px;"> The present search report has been drawn up for all claims </div>			&: member of the same patent family, corresponding document
Place of search		Date of completion of the search	Examiner
The Hague		14-11-1980	MICHIELS