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☒	Claim(s) : paged ...17... to paged ...17...	
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IP03

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REGENERATION OF ACETYLENE CONVERTER
CATALYSTS BY HYDROGEN STRIPPING ✓

BACKGROUND OF THE INVENTION

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Field of the Invention

The present invention relates to an improved method for regenerating catalysts that have been used to remove acetylenic contaminants from olefin product streams. More particularly, the present invention relates to an improved method for regenerating palladium-containing catalysts that have been used to remove acetylenic contaminants from ethylene.

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Product streams of liquid or liquefiable olefins and diolefins typically are contaminated with small amounts of acetylenic impurities. For example, the ethylene/ethane fraction in an ethylene plant typically contains 0.5 - 2.0% acetylenic impurities. Such acetylenic contamination is undesirable because acetylene tends to poison the catalysts that are used to convert ethylene to polyethylene. Acetylene also can form metal acetylides which are explosive and which may contaminate the equipment that is used to process such product streams.

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It is known that acetylenic impurities can be selectively hydrogenated and thereby removed from such a product streams by passing the product stream over a catalyst (an "acetylene hydrogenation catalyst") in the presence of hydrogen; however, the hydrogenation process typically results in the deposition of a green oil on the catalyst which deactivates the catalyst.

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Therefore, acetylene hydrogenation processes typically include an oxygenation step or a "burn" step to remove the deactivating carbonaceous residues from the catalyst followed by a hydrogen reduction step to
5 reactivate the catalyst. See, e.g., US-A-3,812,057 (Morgan) and US-A-4,424,255 (Toyoda).

An oxygenation step followed by hydrogen reduction normally is effective to regenerate an
10 acetylene hydrogenation catalyst; however, there are many disadvantages to the use of an oxygenation step during regeneration of such catalysts.

First, when oxygen and hydrogen come together
15 under the conditions used to regenerate the catalyst, an exothermic reaction is produced which may result in uncontrolled temperature runaway. Thus, before the regeneration is performed, it is necessary to purge the catalyst of hydrogen and hydrocarbons using an
20 inert gas, such as nitrogen gas, both before and after the oxygen-containing stream is introduced. The purging process is both tedious and time consuming. Furthermore, if the regeneration is performed in situ, the concentration of oxygen in the regeneration gas
25 stream must be regulated carefully in order to avoid reactor temperature run-away. It would be advantageous if acetylene hydrogenation catalysts could be regenerated using a method which did not require such time consuming purging and monitoring.

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The use of an oxygenation step during regeneration of an acetylene hydrogenation catalyst also presents an environmental concern due to the resulting emission of carbon monoxide, carbon dioxide,

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and unburned hydrocarbons. The hydrocarbon residue that remains on the catalyst can comprise up to 10 wt% of the catalyst. The oxygenation of this amount of residue results in the emission of a substantial amount of carbon monoxide and carbon dioxide. In addition, the emission during oxygenation may contain approximately 6-10% of unburned hydrocarbons. It would be advantageous if acetylene reduction catalysts could be regenerated in a manner that did not result in such environmentally undesirable emissions.

Regeneration of acetylene hydrogenation catalysts using an oxygenation step also is undesirable because the oxygenation step has a negative impact on the life of the catalyst. A catalyst that has been used to hydrogenate acetylene typically must be regenerated once every one to three months. Acetylene hydrogenation catalysts are heat sensitive, and exposure to excessive heat decreases the activity of the catalyst. The oxygenation step that is used in most regeneration processes typically is run at temperatures between 371-455°C (700-850°F). The exposure of an acetylene hydrogenation catalyst to such high temperatures at such regular intervals takes a great toll on the life of the catalyst. It would be advantageous if the regeneration of such catalysts could take place at lower temperatures which reduced the thermal stress induced during the regeneration.

Some of these disadvantages can be avoided if the catalyst is regenerated ex situ, or outside of the reactor. However, the unloading and reloading of the reactor with the catalyst is a time consuming process. Even if the regeneration process is performed ex situ,

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the catalyst still must be purged with an inert gas both before unloading and after reloading the reactor. Thus, regardless of where the regeneration process takes place, significant reactor down time is required if the catalyst is regenerated using a process that includes an oxidation step.

For all of these reasons, it would be advantageous if acetylene reducing catalysts could be regenerated without an oxygenation step. Col. 4, lines 16-35 of US-A-3,912,789 acknowledges that partial regeneration can be accomplished using a hydrogenation step alone. However, this patent teaches that full regeneration of an exhausted catalyst requires an oxygenation step. Therefore, a process has yet to be developed that can fully regenerate acetylene reduction catalysts without the need for an oxygenation step.

Not only is an oxygenation step undesirable, but any additional step in the regeneration procedure is undesirable because each step requires a change of conditions and switch over techniques which can be deleterious to the performance or longevity of the regenerated catalyst. For example, GB-1,158,418 teaches a method of regenerating hydrogenation catalysts comprising a hydrocarbon wash step followed by a hydrogen treatment. Indeed this patent discusses an already known method consisting of contacting hydrogen with the catalyst at an elevated temperature (p. 1, line 77 - p. 2, line 10), but reports that this known method was still insufficient to restore completely the initial activity of the selective hydrogenation catalyst.

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US-A-2,946,829 discloses a process of making a Pd/Al₂O₃ catalyst for selective hydrogenation, used with the industry standard method of regeneration, which uses steam to provide heat to attain the needed temperature to burn the polymeric deposits off the catalyst. When a small amount of air is mixed into the steam (see Example 3, col. 5, l. 52-55), the resulting catalyst is relatively free of carbonaceous deposits. The main function of the hydrogen reduction step is to reduce the oxidized metal back to its metallic state. In fact, the hydrogen reduction step is not even required, as shown in Example 3, col. 5, l. 65. On day 17, regeneration 6 did not include a reduction step. The catalyst nevertheless was put back on stream after steam treatment and exhibited very high activity, i.e., at a space velocity of 2,000 and 150°F, acetylene in the reactor outlet dropped from an inlet concentration of 0.35% to 1.3 ppm. This compares favorably to the results of the first regeneration, Example 1, which did use a hydrogen reduction step after steam treatment -- 5 ppm acetylene at the reactor outlet at a much lower space velocity of 1,000 and 130°F.

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In addition, US-A-2,946,829 teaches the need for vigorous regeneration in order to remove polymer deposits. Such severe regeneration leads to a loss of physical strength in the hydrogenation catalyst, or to impaired activity or selectivity (col. 2, lines 30-37). The vigorous step in the disclosure is the step of burning off the polymer deposits in the presence of steam -- not the hydrogen reduction step. Thus, this

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art teaches that the steam treatment step is essential to regeneration of a hydrogenation catalyst.

5 GB-A-907,348 teaches the partial regeneration of a nickel catalyst using a hydrogen treatment. Although a temperature range of 200-600°C is mentioned, all of the actual regenerations described are carried out at temperatures in the range of 204-250°C. In the Provisional Specification of GB-A-10 907,348, temperatures at the lower end of the range are said to be preferred, particularly 200-300°C. From the actual experiments of GB-A-907,348, regeneration at 250°C did not cause recovery of fresh catalyst activity, and the stability of the 15 regenerated catalyst was lower except in the experiment that used the lowest temperature (204°C). (See Examples 1-3.) The failure to recover the activity of fresh catalyst is clear because a higher temperature is required to maintain the same hydrogen 20 consumption during regeneration (Example 1, 127°C fresh v. 143°C regenerated; Example 2, 127°C fresh v. 138°C regenerated). And, in Examples 1 and 2 (which used a regeneration temperature of 250°C), the stability of the regenerated catalyst is lower 25 (Example 1, fresh catalyst required 152°C after 670 hours v. regenerated catalyst required 166°C after 477 hours; Example 2, fresh catalyst required 127°C after 335 hours v. regenerated catalyst required 138°C after 127 hours). However, in Example 3 (which regenerates 30 the catalyst at a temperature of 204°C), although the activity of the fresh catalyst is not completely recovered, the stability of the regenerated catalyst is higher than the stability of the fresh catalyst (regenerated catalyst required 142°C after 1410 hours,

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fresh catalyst required 160°C after 327 hours). Thus this publication teaches away from the regeneration of catalysts using hydrogen at temperatures that are above 250°C.

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SUMMARY OF THE INVENTION

According to the present invention there is provided a method of substantially completely regenerating a catalyst that has been used to remove acetylenic impurities from an olefin stream and which has become at least partially deactivated by that use, which comprises substantially stripping the deactivated catalyst of carbonaceous deposits using hydrogen at a linear velocity of at least 15.2 cm/second (0.5 feet per second), at a temperature of from 315 - 400°C (599 - 750°F) and at other conditions such that substantially complete regeneration is effected, wherein said stripping is essentially the only regeneration treatment employed and occurs in the absence of an oxygenation step.

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It is a feature of the invention that acetylene reduction catalysts can be substantially fully regenerated by hydrogen stripping, alone, at relatively low temperatures which are nevertheless greater than those taught away from in prior art such as GB-A-907,348. It has also been found that palladium-containing catalysts that have been used to purify ethylene unexpectedly have a better selectivity to ethylene after they are hydrogen stripped according to the present invention.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a chart showing the Temperature Programmed Oxidation (TPO) spectra of the UCI G58B

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catalyst of Example 1 before (a) and after (b) hydrogen stripping.

Fig. 2 is a bar graph comparing the catalyst activity of the BASF H011 catalyst of Example 2 before and after hydrogen stripping. "SOR" under the first bar in the graph stands for activity at the start of the run. "EOR" under the second bar in the graph stands for activity at the end of the run. The bar above "662°F H₂" represents the activity of the substantially completely regenerated catalyst after hydrogen stripping according to the invention at about 350°C (662°F). The bar above "788°F H₂" represents the (reduced) activity of the incompletely regenerated catalyst after further hydrogen stripping outside the scope of the invention at about 420°C (788°F).

Fig. 3(a) is a graph comparing the acetylene conversion activity of the UCI G58E catalyst of Example 3 when fresh to the activity of that same (substantially completely regenerated) catalyst after it has been hydrogen stripped according to the present invention at about 350°C (662°F).

Fig. 3(b) is a graph comparing the deactivation rate of the fresh and stripped catalyst of Example 3.

Fig. 3(c) is a graph comparing the selectivity to ethylene of the fresh and stripped catalyst of Example 3.

Fig. 3(d) is a graph comparing the selectivity to ethane of the fresh and stripped catalyst of Example 3.



Fig. 3(e) is a graph comparing the selectivity to hydrocarbons having four or more carbon atoms of the fresh and stripped catalyst of Example 3.

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DETAILED DESCRIPTION OF THE INVENTION

Preferably the at least partially deactivated (spent) acetylene hydrogenation catalyst is hydrogen stripped with a mixture of hydrogen and inert gas.

10 When pure hydrogen is not used, the hydrogen concentration in such mixtures may be from 0.1 to less than 100%, preferably from 5 to 10%. Since a stripping gas having only 5-10% of hydrogen may be used during the stripping process, any low value

15 hydrogen source, preferably without carbon monoxide, can be employed. For example, hydrogen may be purchased and mixed fresh with an inert gas, or the hydrogen may come from another refining operation. For example, the overhead effluent from a

20 demethanizer, which contains about 5% H_2 in CH_4 (normally used as fuel gas) may be one potential source for hydrogen. It also may be possible to recycle hydrogen that has already been used to regenerate the catalyst.

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The percentage of hydrogen in the gas stripping mixture is not critical to the present invention. In the following examples, a mixture of inert gas and around 9-10% hydrogen was used. Any inert gas may be

30 used in the mixture. The most commonly available and most inexpensive inert gas for use in the invention is nitrogen; therefore, nitrogen is a preferred inert gas for use in the present invention.

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Although the following examples of the invention describe regeneration of palladium based acetylene reduction catalysts, one of skill in the art will recognize that the hydrogen stripping process of the present invention may be used to regenerate other types of catalysts that are used to hydrogenate acetylene. For example the present process could be used to regenerate acetylene hydrogenation catalysts which contain: Group VIII metals, such as nickel, cobalt, ruthenium, palladium, and platinum; Group VIB metals, such as chromium, molybdenum, and tungsten; or Group IB metals, such as copper, silver, or gold. However, the preferred catalyst for use in the present invention is a catalyst in which the primary active element is palladium, preferably one where palladium comprises approximately 0.01-0.5% by weight of the catalyst, more preferably 0.02-0.05%. A palladium content higher than about 0.5% could deteriorate at the temperatures used in the process of the present invention. Optionally the palladium may be combined with another metal, such as silver.

The catalyst metal is typically carried on a support such as silica or alumina.

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The stripping procedure of the invention takes place at a temperature of from 315-400°C (600-750°F), preferably between about 315-372°C (600-700°F), and more preferably at about 350°C (662°F). In order to avoid deactivating the catalyst, especially a palladium based catalyst, or agglomerating the palladium, the temperature of the hydrogen stripping procedure should not exceed about 400°C. The temperature should be at least 315°C to achieve the

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substantially complete regeneration which is commercially desirable, and other process conditions will be readily determinable to enable this objective to be reached.

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The pressure at which the stripping takes place may not be critical; however, the stripping preferably takes place between atmospheric pressure (0 psig) and 2.07 MPag (300 psig), and more preferably between atmospheric pressure and 345 kPag (50 psig). Lower cost hydrogen sources having a low content of hydrogen typically are more readily available at lower pressures. In the following examples, pressures of about 2.07 MPag and atmospheric pressure were used. Similarly, the time period required for stripping is not critical, save it should be sufficient to achieve substantially complete regeneration. One of skill in the art will recognize that the amount of time needed for the stripping procedure can be determined by monitoring the amount of hydrocarbon present in the catalyst until a minimum plateau level has been achieved. In the following examples, the stripping time ranged between 16-24 hrs.

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The flow rate of the hydrogen through the catalyst should be such that the linear velocity through the catalyst should be at least about 15.2 cm/second (0.5 feet/second). This will ensure uniformity of reactant concentrations and temperatures throughout the reactor during regeneration. It has been found that lower velocities may be insufficient to achieve uniform regeneration of the catalyst. The parameter of linear velocity is used herein rather than, e.g., space velocity because linear velocity

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commonly is used to calculate dispersion and mixing phenomena in packed beds. For example, the axial and radial dispersion of reactant concentration are estimated by calculating Peclet numbers (James Carberry, "Chemical and Catalytic Reaction Engineering", p. 162). The linear velocity also is an important factor in controlling heat transfer in the reactor. Furthermore, linear velocities may differ even where the space velocity remains the same. For example, wide and shallow beds will have lower linear velocities than narrow and deep beds will have. However, narrow and deep beds will have a higher pressure drop than wide and shallow beds. Thus, it is desirable to specify either linear velocity or space velocity with the reactor L/D ratio to ensure proper design or scale up of the reactor.

It is a feature of the invention that substantially complete regeneration is achieved without the need for an additional or associated regeneration step, e.g., hydrocarbon wash or steam treat or, particularly, oxygenation. As shown in Example 1 which follows, the process of the invention enables catalyst to be re-used as fresh catalyst after regular hydrogen only regenerations of the catalytic metal sites, preferably in situ in the acetylene reduction reactor. Nevertheless it may be desirable from time to time to clean carbonaceous deposits from the support (as opposed to the catalyst metal) because hydrogen stripping does not remove all of the carbonaceous deposits from the support. Thus it is possible that an air burn may be desirable eventually in order to clean the support to prevent restriction of flow rate, pressure, etc. However, the number of



air burns that may be employed to clean the supports in such a system will be much less than the frequent air burns that heretofore have been required to regenerate the catalyst. An infrequent air burn to
5 clean the support will be much less intrusive and damaging than the frequent, repetitive air burns required in current catalyst regeneration processes.

10 The following examples illustrates the invention.

EXAMPLE 1

An aliquot of UCI G58B catalyst ($\text{Pd}/\text{Al}_2\text{O}_3$), deactivated after 200 hours of use as an acetylene hydrogenation catalyst in olefin stream treatment, was
15 stripped with 10% H_2/Ar at linear velocity greater than 15.2 cm/sec and at a temperature which rose from room temperature to about 750°C (1382°F) at a heating rate of about 13 degrees C/min ($23.4^\circ\text{F}/\text{min}$). The carbonaceous residues on the catalyst were analyzed
20 both before and after hydrogen stripping by temperature programmed oxidation (TPO), which detected carbon oxide emission during the TPO burn while the reactor temperature was linearly increased. The TPO spectra of the spent catalyst before and after
25 hydrogen stripping were plotted as Figure 1(a) and (b), respectively.

Before hydrogen stripping, two types of carbonaceous residues were present on the catalyst. A
30 peak at about 400°C (750°F) represents carbonaceous residues that were present on and/or near palladium. A peak at about 510°C (950°F) represents carbonaceous residues that were present on the support. After hydrogen stripping, only one peak appeared at 550°C



(1022°F). The presence of only this single peak after hydrogen stripping indicated that the carbonaceous residues that were on and/or near the palladium were removed by the hydrogen stripping. Since acetylene conversion occurs mainly on palladium sites in the catalyst, the removal of carbonaceous residues from the palladium can re-expose the palladium active sites and recover substantially all the activity of the palladium. The hydrocarbons that are stripped off the catalyst can be either recycled to the cracker or used as fuel gas.

EXAMPLE 2

A BASF H011 catalyst (Pd/SiO₂) was subjected for 200 hours to the reaction conditions of 1.5% wt C₂H₂ (in an olefinic stream), 1.6 H₂/C₂H₂ molar ratio, 4000 gas hourly space velocity (GHSV), 2.07 MPag (300 psig), and about 66°C (151°F) average bed temperature. After 200 hours, the acetylene conversion of the catalyst decreased from 79% to 58%. The spent catalyst was then regenerated by hydrogen stripping for 16 hours with 5% H₂/N₂ at 2.07 MPag (300 psig) and greater than 15.2 cm/sec linear velocity in the reactor, and about 350°C (662°F). After the hydrogen stripping, the acetylene conversion of the catalyst was 78%. A comparison of the catalyst activity before and after hydrogen stripping is plotted in Figure 2. The results indicate that the hydrogen stripping at about 350°C (662°F) substantially fully regenerated the catalyst.

The temperature used during hydrogen stripping is preferably not too high or else the palladium will begin to agglomerate and will not achieve



substantially complete regeneration using only a hydrogen treat step. For example, when the catalyst was further hydrogen stripped at about 420°C (788°F) for 16 hours, under otherwise the same conditions, the activity of the catalyst was reduced to 62% acetylene conversion -- a dramatic decrease in catalyst activity.

EXAMPLE 3

A spent UCI G58E catalyst (Pd/Ag/Al₂O₃) which had been used for acetylene hydrogenation in an ethylene stream was hydrogen stripped at about 350°C (662°F) and 1 atmosphere pressure with 9% H₂/N₂ at linear velocity in the reactor of greater than 15.2 cm/sec, for 24 hours. The performance of the hydrogen stripped catalyst was then compared to the performance of fresh catalyst at 70 hours into the activity test. The results are tabulated in Table I. The parameters of the activity test carried out in a normal hydrogenation reactor were 1.4% wt C₂H₂, 1.2 H₂/C₂H₂ molar ratio, 4900 GHSV, 2.07 MPag (300 psig), about 102°C (215°F) sand-bath temperature.

TABLE I

	<u>Fresh</u>	<u>H₂ Stripped</u>
C ₂ H ₂ Conversion	80%	80%
Selectivity to C ₂ H ₄	57%	67%
Selectivity to C ₂ H ₆	32%	23%
Selectivity to C ₄ +	11%	10%
Deactivation Rate	-0.1%/hr	-0.2%/hr

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As seen from Table I, the spent catalyst which had been hydrogen stripped according to the invention unexpectedly had a selectivity to ethylene that was 10 points better than the selectivity of the fresh catalyst. Also, the ethane make was substantially reduced after hydrogen stripping. This result suggests that a "de-edging" process may have occurred which reduced the number of palladium sites responsible for over hydrogenating acetylene/ethylene to ethane.

Although the deactivation rate was higher for the hydrogen stripped catalyst, the deactivation rate can be overcome by more frequent hydrogen stripping. Even if more frequent hydrogen stripping is required to regenerate catalyst, the present process may be less time consuming and less damaging to the catalyst than frequent air burns or other additional treatment steps.

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**CLAIMS:**

1. A method of substantially completely
regenerating a catalyst that has been used to remove
5 acetylenic impurities from an olefin stream and which
has become at least partially deactivated by that use,
which comprises substantially stripping the
deactivated catalyst of carbonaceous deposits using
hydrogen at a linear velocity of at least 15.2
10 cm/second (0.5 feet per second), at a temperature of
from 315 - 400°C (599 - 750°F) and at other conditions
such that substantially complete regeneration is
effected, wherein said stripping is essentially the
only regeneration treatment employed and occurs in the
15 absence of an oxygenation step.

2. The method of claim 1 wherein the
temperature is from 315 - 372°C (600 - 700°F),
preferably about 350°C (662°F).

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3. The method of claim 1 or 2 wherein the
hydrogen stripping employs a gas comprising an inert
gas, preferably nitrogen, and from 5 to 10% of
hydrogen.

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4. The method of any preceding claim wherein
the catalyst comprises palladium, optionally together
with another metal.

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5. The method of claim 4 wherein the palladium
comprises from 0.01 to 0.5 wt%, preferably from 0.02
to 0.05% of the catalyst.



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6. The method of any preceding claim wherein the catalyst has been used to remove acetylenic impurities from ethylene.

5 7. The method of claim 6 wherein after regeneration the catalyst is used to remove acetylenic impurities from ethylene and the selectivity of the catalyst to ethylene is enhanced.

10 8. The method of any preceding claim wherein the catalyst comprises a silica or alumina support.



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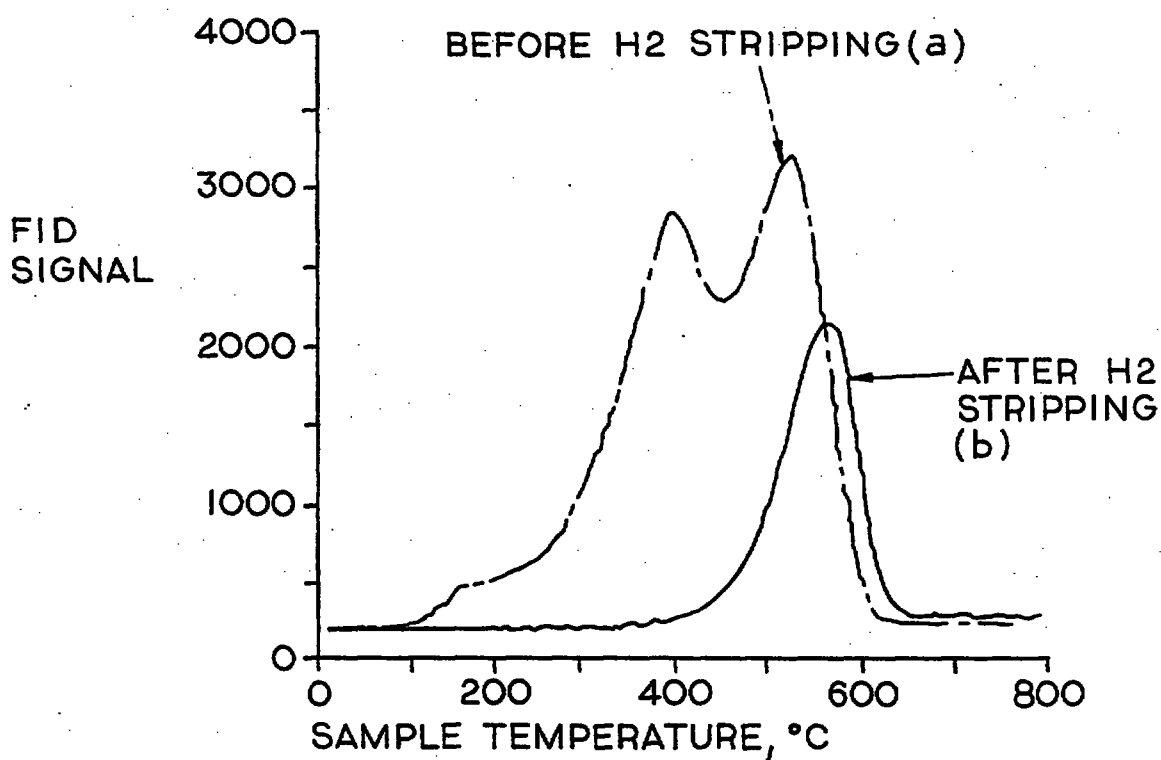


FIG. 1

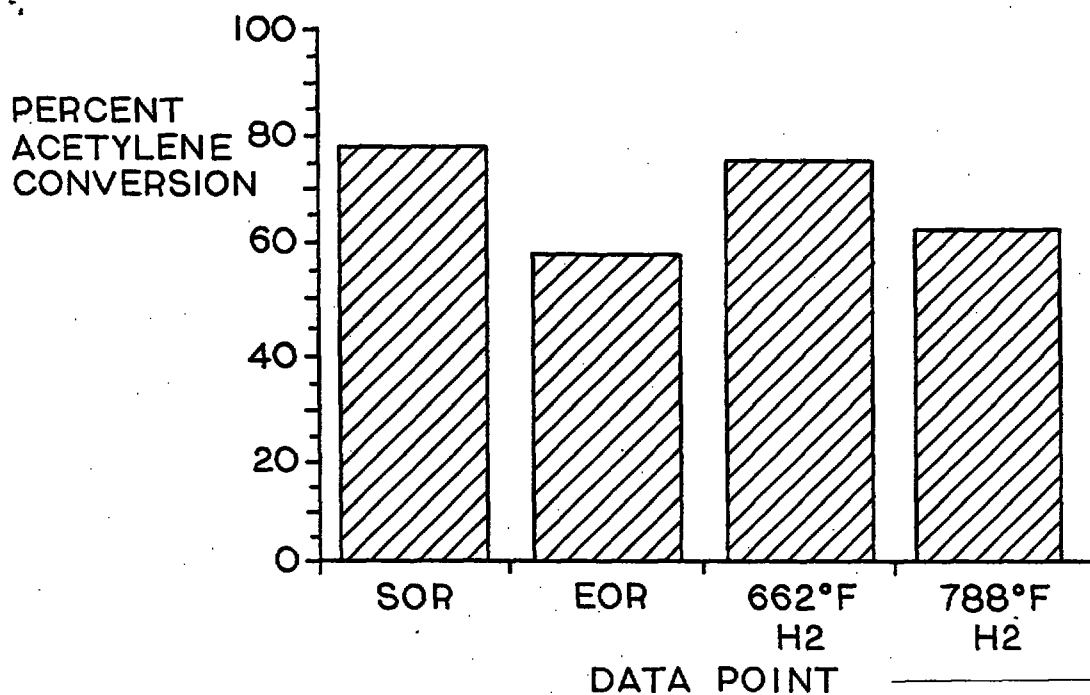


FIG. 2

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SUBSTITUTE SHEET

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UCI G58E
1.2 H₂/C₂H₂, 1.4 % C₂H₂,
4900 GHSV, 300 PSI, 215 °F

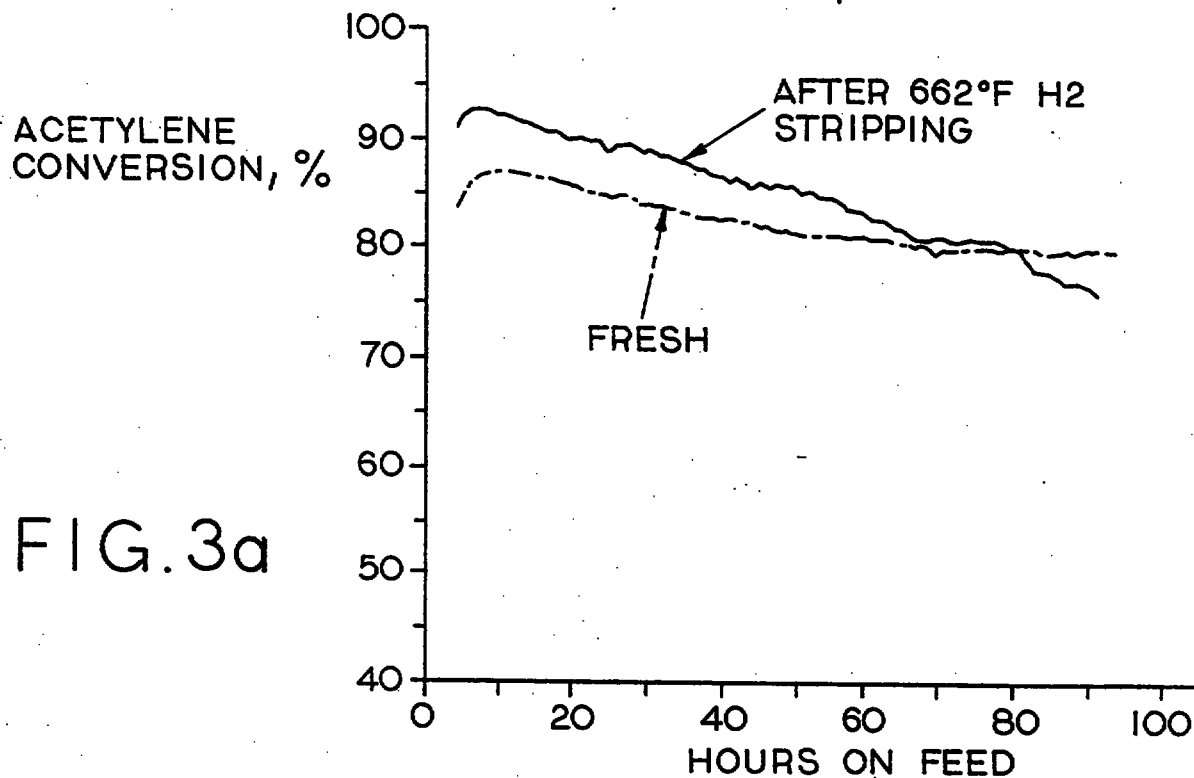


FIG. 3a

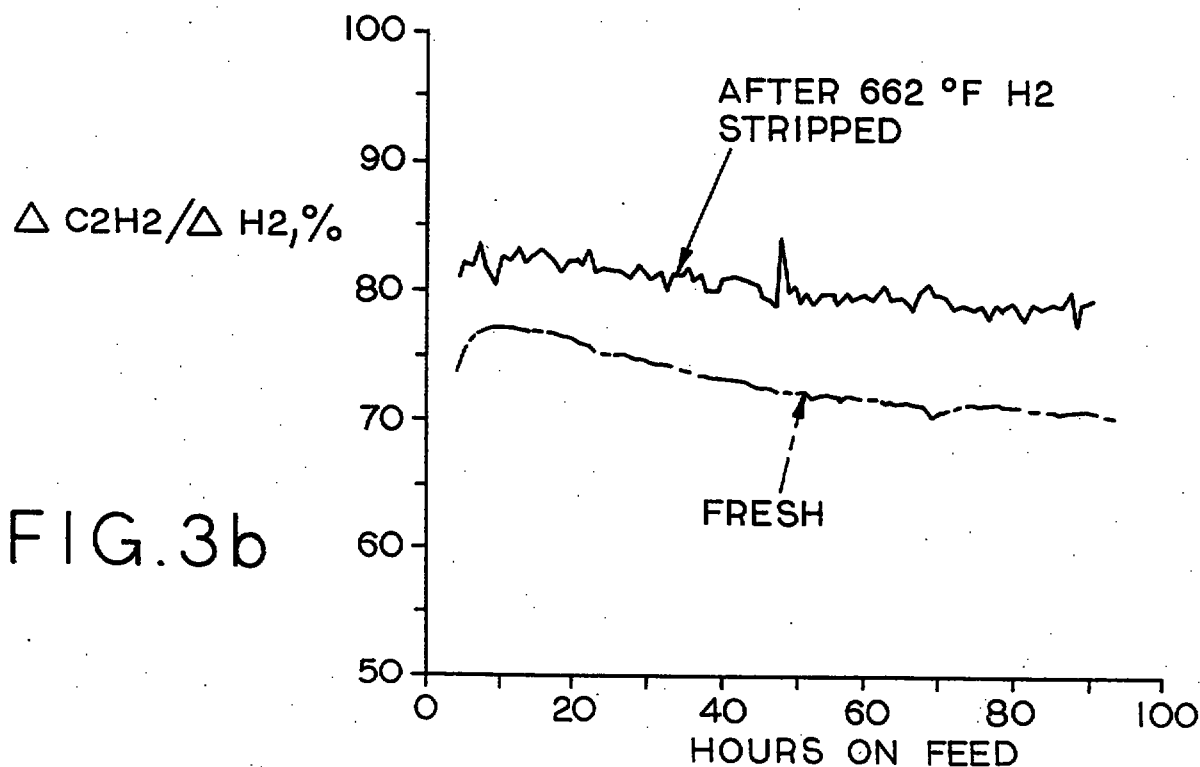


FIG. 3b

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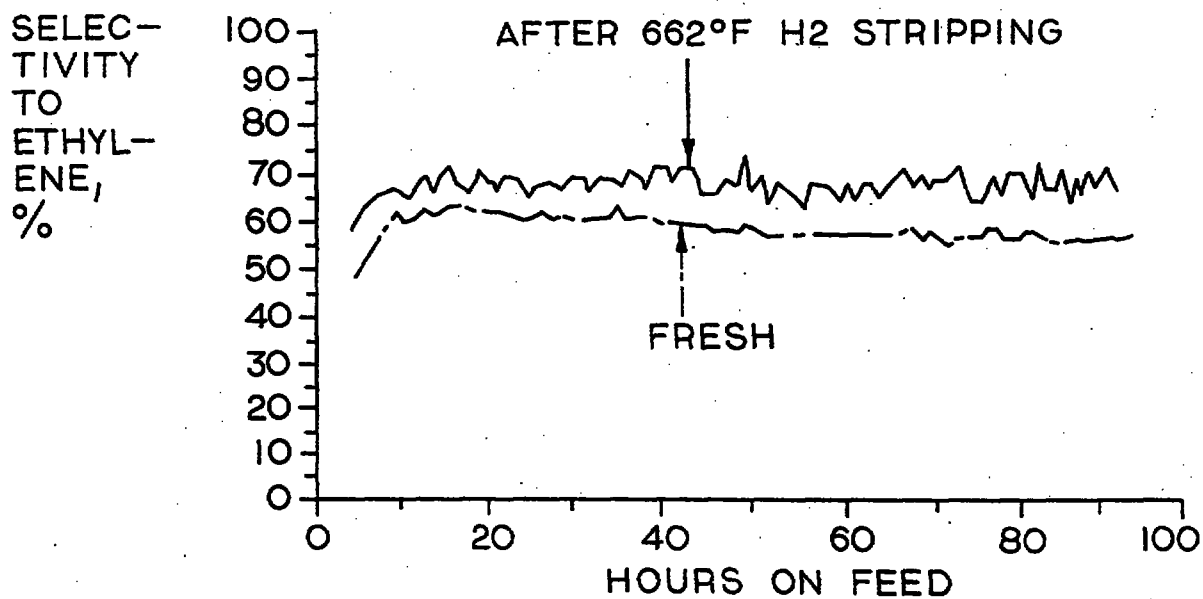


FIG. 3c

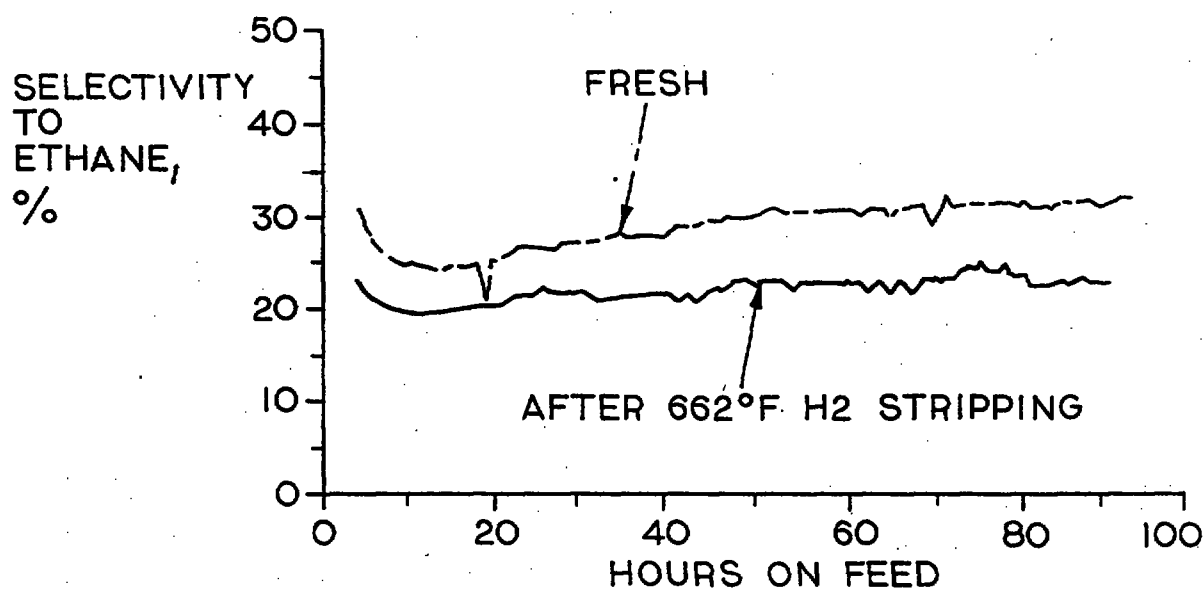
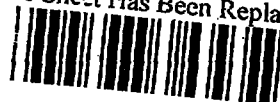


FIG. 3d

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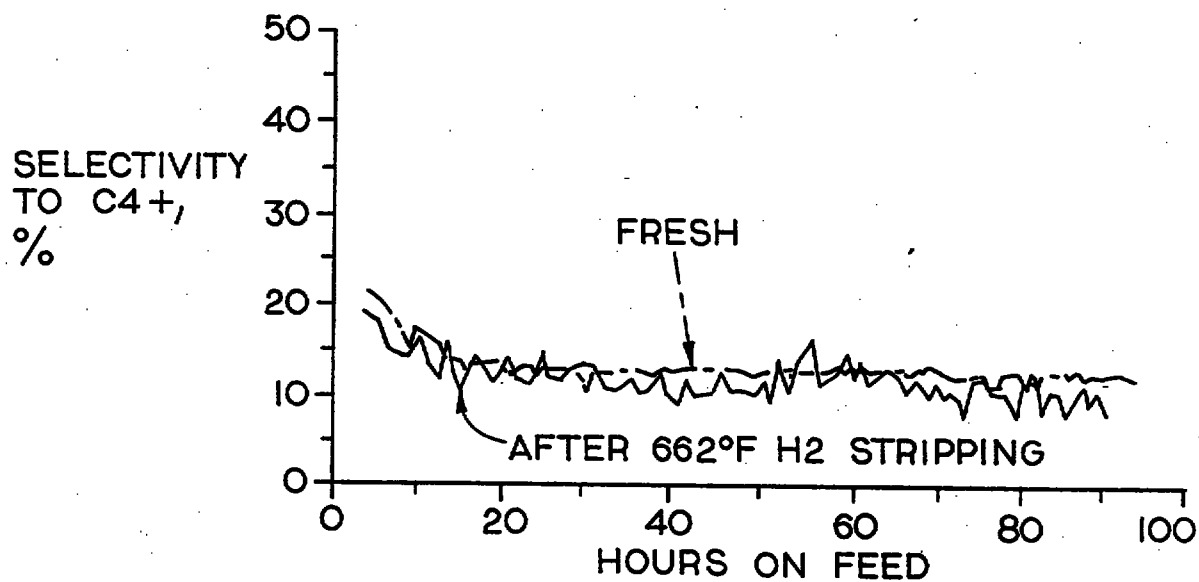


FIG. 3e

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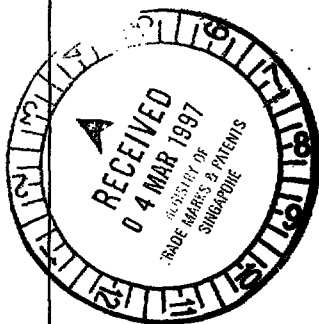
2-8210038

The Registrar of Patents
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REQUEST FOR THE GRANT OF A PATENT

THE GRANT OF A PATENT IS REQUESTED BY THE UNDERSIGNED ON THE
BASIS OF THE PRESENT APPLICATION

I. Applicants Reference	MH/CLH /ptkp/PAT/8007857	
II. Title of Invention	REGENERATION OF ACETYLENE CONVERTER CATALYSTS BY HYDROGEN STRIPPING	
III. Applicant(s) (see note 2)	(a) Name	EXXON CHEMICAL PATENTS INC.
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	(b) Name	_____
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	City	
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	Country	
	(c) Name	_____
	Street Name & Number	
	City	
	State	
	Country	



IV. Inventors <i>(See note 3)</i> (a) The applicant(s) is/are the sole/joint inventor(s). (b) A statement on Patents Form 8 is XXXX furnished.	<table border="0"> <tr> <td>☐</td> <td>Yes</td> <td>☒</td> <td>No</td> </tr> <tr> <td>☒</td> <td>Yes</td> <td>☐</td> <td>No</td> </tr> </table>				☐	Yes	☒	No	☒	Yes	☐	No
☐	Yes	☒	No									
☒	Yes	☐	No									
V. Name of Agent (if any) <i>(See note 4)</i>	DREW & NAPIER											
VI. Address for Service <i>(See note 5)</i>	Block/Hse No			Level No								
	Unit No/PO Box	152		Postal Code	900302							
	Street Name	Robinson Road										
	Building Name											
VII. Declaration of Priority <i>(See note 6)</i>	(a) Country	UNITED STATES OF AMERICA										
	Filing Date	19	JUN	1992	File No 07/901,321							
	(b) Country											
	Filing Date	0		0	File No							
	(c) Country											
	Filing Date	0		0	File No							
	IPC Symbols(s)	B01J 23/96, 38/10, C07C 7/167										
VIII. Claiming an earlier filing date under section 20(3), 26(6) or 47(4). <i>(See note 7)</i>	Application No	---										
	Filing Date											
IX. Invention has been displayed at an International Exhibition <i>(See note 8)</i>	<table border="0"> <tr> <td>☐</td> <td>Yes</td> <td>☒</td> <td>No</td> </tr> </table>					☐	Yes	☒	No			
☐	Yes	☒	No									

X. Claiming an earlier filing date and priority date under section 116(6) <i>(See note 9)</i>	Application No	93914629.4		
	Office File in	EUROPEAN PATENT OFFICE		
	Filing Date	18	JUN	1993
	Priority Date	19	JUN	1992
	I/We declare that the earlier application was still pending on			
	Date Pending	23	FEB	1995
XI. Section 114 requirements <i>(See note 10)</i>	The invention relates to and/or uses a micro-organism deposited for the purposes of disclosure in accordance with section 114 with a depository authority under the Budapest Treaty. ☐ Yes ☒ No			
XII. Check List <i>(To be filled in by applicant or agent)</i>	A. The application contains the following number of sheet(s) :-			
	1. Request.	4		sheets
	2. Description.	16		sheets
	3. Claim(s).	2		sheets
	4. Drawing(s).	4		sheets
	5. Abstract.	1		sheets
	B. The application as filed is accompanied by :-			
	1. Priority document.	X		
	2. Translation of priority document.			
	3. Statement of Inventorship & right to grant.	X		
	4. International Exhibition Certificate.			
	5. Copy of receipt issued by an international depository institution under rule 7 of the regulations under the Budapest Treaty.			
	6. Translation of receipt.			
XIII. Signature(s) <i>(See note 11)</i>	Applicant (a)	DREW & NAPIER		
	Date	22 FEB 1996		
	Applicant (b)			
	Date			
	Applicant (c)			
	Date			

NOTES:

1. This form when completed, should be brought or sent to the Registry of Patents together with the prescribed fee and 3 copies of the description of the invention, and of any drawings.
2. Enter the name and address of each applicant in the space provided at paragraph II. Names of individuals should be indicated in full and the surname or family name should be underlined. The names of all partners in a firm must be given in full. Bodies corporate should be designated by their corporate name and country of incorporation and, where appropriate, the state of incorporation within that country should be entered where provided. Where more than three applicants are to be named, the names and addresses of the fourth and any further applicants should be given on a separate sheet attached to this Form together with signature of each of these further applicants.
3. Where the applicant or applicants is/are the sole inventor or the joint inventors, paragraph IV should be completed by marking the "YES" Box in the declaration (a) and the "NO" Box in the alternative statement (b). Where this is not the case, the "NO" Box in declaration (a) should be marked and a statement will be required to be filed on Patents Form 8.
4. If the applicant has appointed an agent to act on his behalf, the agent's name should be indicated in the spaces available in paragraphs V.
5. An address for service in Singapore to which all documents may be sent must be stated at paragraph VI. It is recommended that a telephone number be provided if an agent is not appointed.
6. The declaration of priority at paragraph VII should state the date of the previous filing and the country in which it was made and indicate the file number, if available. The symbols of the International Patent Classification allocated to the priority application should also be stated, if available.
7. When an application is made by virtue of section 20(3), 26(6), or 47(4), the appropriate section should be identified at paragraph VIII and the number of the earlier application or any patent granted thereon identified.
8. Where the applicant wishes an earlier disclosure of the invention by him at an International Exhibition to be disregarded in accordance with section 14(4)(c), then the "YES" box at paragraph IX should be marked. Otherwise the "NO" box should be marked.
9. When the application is made by virtue of section 116(6), the applicant should complete the Declaration at paragraph VII and give the details required at paragraph X in respect of the earlier application filed either at the UK Patent Office or the European Patent Office (including the earliest declared priority date in respect of that application). The Declaration at paragraph X should also be completed.
10. Where in disclosing the invention the application refers to one or more micro-organisms deposited with a depository authority under the Budapest Treaty, then the "YES" box at paragraph XI should be marked. Otherwise the "NO" box should be marked.
11. Attention is drawn to rules 95 and 110 of the Patent Rules 1995. Where there are more than three applicants, see also Note 2 above.
12. Applicants resident in Singapore are reminded that if the Registry of Patents considers that an application contains information the publication of which might be prejudicial to the defence of Singapore or the safety of the public, it may prohibit or restrict its publication or communication. Any person resident in Singapore and wishing to apply for a patent protection in other countries must first obtain permission from the Singapore Registry of Patents unless they have already applied for a patent for the same invention in Singapore. In the latter case, no application should be made overseas until at least two months after the application had been filed in Singapore.

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REGENERATION OF ACETYLENE CONVERTER

CATALYSTS BY HYDROGEN STRIPPING

BACKGROUND OF THE INVENTION

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Field of the Invention

The present invention relates to an improved method for regenerating catalysts that have been used to remove acetylenic contaminants from olefin product streams. More particularly, the present invention relates to an improved method for regenerating palladium-containing catalysts that have been used to remove acetylenic contaminants from ethylene.

Product streams of liquid or liquefiable olefins and diolefins typically are contaminated with small amounts of acetylenic impurities. For example, the ethylene/ethane fraction in an ethylene plant typically contains 0.5 - 2.0% acetylenic impurities. Such acetylenic contamination is undesirable because acetylene tends to poison the catalysts that are used to convert ethylene to polyethylene. Acetylene also can form metal acetylides which are explosive and which may contaminate the equipment that is used to process such product streams.

It is known that acetylenic impurities can be selectively hydrogenated and thereby removed from such a product streams by passing the product stream over a catalyst (an "acetylene hydrogenation catalyst") in the presence of hydrogen; however, the hydrogenation process typically results in the deposition of a green oil on the catalyst which deactivates the catalyst.

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Therefore, acetylene hydrogenation processes typically include an oxygenation step or a "burn" step to remove the deactivating carbonaceous residues from the catalyst followed by a hydrogen reduction step to reactivate the catalyst. See, e.g., US-A-3,812,057 (Morgan) and US-A-4,424,255 (Toyoda).

An oxygenation step followed by hydrogen reduction normally is effective to regenerate an acetylene hydrogenation catalyst; however, there are many disadvantages to the use of an oxygenation step during regeneration of such catalysts.

First, when oxygen and hydrogen come together under the conditions used to regenerate the catalyst, an exothermic reaction is produced which may result in uncontrolled temperature runaway. Thus, before the regeneration is performed, it is necessary to purge the catalyst of hydrogen and hydrocarbons using an inert gas, such as nitrogen gas, both before and after the oxygen-containing stream is introduced. The purging process is both tedious and time consuming. Furthermore, if the regeneration is performed in situ, the concentration of oxygen in the regeneration gas stream must be regulated carefully in order to avoid reactor temperature run-away. It would be advantageous if acetylene hydrogenation catalysts could be regenerated using a method which did not require such time consuming purging and monitoring.

The use of an oxygenation step during regeneration of an acetylene hydrogenation catalyst also presents an environmental concern due to the resulting emission of carbon monoxide, carbon dioxide,

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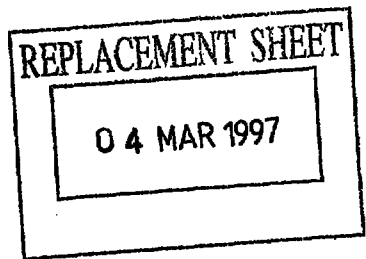
and unburned hydrocarbons. The hydrocarbon residue that remains on the catalyst can comprise up to 10 wt% of the catalyst. The oxygenation of this amount of residue results in the emission of a substantial amount of carbon monoxide and carbon dioxide. In addition, the emission during oxygenation may contain approximately 6-10% of unburned hydrocarbons. It would be advantageous if acetylene reduction catalysts could be regenerated in a manner that did not result in such environmentally undesirable emissions.

Regeneration of acetylene hydrogenation catalysts using an oxygenation step also is undesirable because the oxygenation step has a negative impact on the life of the catalyst. A catalyst that has been used to hydrogenate acetylene typically must be regenerated once every one to three months. Acetylene hydrogenation catalysts are heat sensitive, and exposure to excessive heat decreases the activity of the catalyst. The oxygenation step that is used in most regeneration processes typically is run at temperatures between 371-455°C (700-850°F). The exposure of an acetylene hydrogenation catalyst to such high temperatures at such regular intervals takes a great toll on the life of the catalyst. It would be advantageous if the regeneration of such catalysts could take place at lower temperatures which reduced the thermal stress induced during the regeneration.

Some of these disadvantages can be avoided if the catalyst is regenerated ex situ, or outside of the reactor. However, the unloading and reloading of the reactor with the catalyst is a time consuming process. Even if the regeneration process is performed ex situ,

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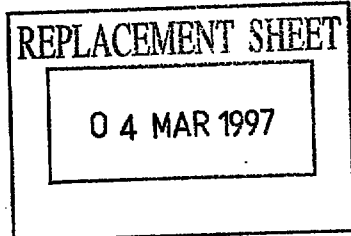
the catalyst still must be purged with an inert gas both before unloading and after reloading the reactor. Thus, regardless of where the regeneration process takes place, significant reactor down time is required if the catalyst is regenerated using a process that includes an oxidation step.

For all of these reasons, it would be advantageous if acetylene reducing catalysts could be regenerated without an oxygenation step. Col. 4, lines 16-35 of US-A-3,912,789 acknowledges that partial regeneration can be accomplished using a hydrogenation step alone. However, this patent teaches that full regeneration of an exhausted catalyst requires an oxygenation step. Therefore, a process has yet to be developed that can fully regenerate acetylene reduction catalysts without the need for an oxygenation step.

Not only is an oxygenation step undesirable, but any additional step in the regeneration procedure is undesirable because each step requires a change of conditions and switch over techniques which can be deleterious to the performance or longevity of the regenerated catalyst. For example, GB-1,158,418 teaches a method of regenerating hydrogenation catalysts comprising a hydrocarbon wash step followed by a hydrogen treatment. Indeed this patent discusses an already known method consisting of contacting hydrogen with the catalyst at an elevated temperature (p. 1, line 77 - p. 2, line 10), but reports that this known method was still insufficient to restore completely the initial activity of the selective hydrogenation catalyst.

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US-A-2,946,829 discloses a process of making a Pd/Al₂O₃ catalyst for selective hydrogenation, used with the industry standard method of regeneration, which uses steam to provide heat to attain the needed temperature to burn the polymeric deposits off the catalyst. When a small amount of air is mixed into the steam (see Example 3, col. 5, l. 52-55), the resulting catalyst is relatively free of carbonaceous deposits. The main function of the hydrogen reduction step is to reduce the oxidized metal back to its metallic state. In fact, the hydrogen reduction step is not even required, as shown in Example 3, col. 5, l. 65. On day 17, regeneration 6 did not include a reduction step. The catalyst nevertheless was put back on stream after steam treatment and exhibited very high activity, i.e., at a space velocity of 2,000 and 150°F, acetylene in the reactor outlet dropped from an inlet concentration of 0.35% to 1.3 ppm. This compares favorably to the results of the first regeneration, Example 1, which did use a hydrogen reduction step after steam treatment -- 5 ppm acetylene at the reactor outlet at a much lower space velocity of 1,000 and 130°F.

In addition, US-A-2,946,829 teaches the need for vigorous regeneration in order to remove polymer deposits. Such severe regeneration leads to a loss of physical strength in the hydrogenation catalyst, or to impaired activity or selectivity (col. 2, lines 30-37). The vigorous step in the disclosure is the step of burning off the polymer deposits in the presence of steam -- not the hydrogen reduction step. Thus, this

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art teaches that the steam treatment step is essential to regeneration of a hydrogenation catalyst.

GB-A-907,348 teaches the partial regeneration of a nickel catalyst using a hydrogen treatment. Although a temperature range of 200-600°C is mentioned, all of the actual regenerations described are carried out at temperatures in the range of 204-250°C. In the Provisional Specification of GB-A-907,348, temperatures at the lower end of the range are said to be preferred, particularly 200-300°C. From the actual experiments of GB-A-907,348, regeneration at 250°C did not cause recovery of fresh catalyst activity, and the stability of the regenerated catalyst was lower except in the experiment that used the lowest temperature (204°C). (See Examples 1-3.) The failure to recover the activity of fresh catalyst is clear because a higher temperature is required to maintain the same hydrogen consumption during regeneration (Example 1, 127°C fresh v. 143°C regenerated; Example 2, 127°C fresh v. 138°C regenerated). And, in Examples 1 and 2 (which used a regeneration temperature of 250°C), the stability of the regenerated catalyst is lower (Example 1, fresh catalyst required 152°C after 670 hours v. regenerated catalyst required 166°C after 477 hours; Example 2, fresh catalyst required 127°C after 335 hours v. regenerated catalyst required 138°C after 127 hours). However, in Example 3 (which regenerates the catalyst at a temperature of 204°C), although the activity of the fresh catalyst is not completely recovered, the stability of the regenerated catalyst is higher than the stability of the fresh catalyst (regenerated catalyst required 142°C after 1410 hours,



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fresh catalyst required 160°C after 327 hours). Thus this publication teaches away from the regeneration of catalysts using hydrogen at temperatures that are above 250°C.

SUMMARY OF THE INVENTION

According to the present invention there is provided a method of substantially completely regenerating a catalyst that has been used to remove acetylenic impurities from an olefin stream and which has become at least partially deactivated by that use, which comprises substantially stripping the deactivated catalyst of carbonaceous deposits using hydrogen at a linear velocity of at least 15.2 cm/second (0.5 feet per second), at a temperature of from 315 - 400°C (599 - 750°F) and at other conditions such that substantially complete regeneration is effected, wherein said stripping is essentially the only regeneration treatment employed and occurs in the absence of an oxygenation step.

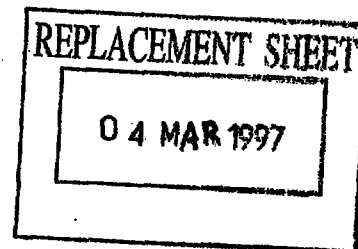
It is a feature of the invention that acetylene reduction catalysts can be substantially fully regenerated by hydrogen stripping, alone, at relatively low temperatures which are nevertheless greater than those taught away from in prior art such as GB-A-907,348. It has also been found that palladium-containing catalysts that have been used to purify ethylene unexpectedly have a better selectivity to ethylene after they are hydrogen stripped according to the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a chart showing the Temperature Programmed Oxidation (TPO) spectra of the UCI G58B

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catalyst of Example 1 before (a) and after (b) hydrogen stripping.

Fig. 2 is a bar graph comparing the catalyst activity of the BASF H011 catalyst of Example 2 before and after hydrogen stripping. "SOR" under the first bar in the graph stands for activity at the start of the run. "EOR" under the second bar in the graph stands for activity at the end of the run. The bar above "662°F H₂" represents the activity of the substantially completely regenerated catalyst after hydrogen stripping according to the invention at about 350°C (662°F). The bar above "788°F H₂" represents the (reduced) activity of the incompletely regenerated catalyst after further hydrogen stripping outside the scope of the invention at about 420°C (788°F).

Fig. 3(a) is a graph comparing the acetylene conversion activity of the UCI G58E catalyst of Example 3 when fresh to the activity of that same (substantially completely regenerated) catalyst after it has been hydrogen stripped according to the present invention at about 350°C (662°F).

Fig. 3(b) is a graph comparing the deactivation rate of the fresh and stripped catalyst of Example 3.

Fig. 3(c) is a graph comparing the selectivity to ethylene of the fresh and stripped catalyst of Example 3.

Fig. 3(d) is a graph comparing the selectivity to ethane of the fresh and stripped catalyst of Example 3.



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Fig. 3(e) is a graph comparing the selectivity to hydrocarbons having four or more carbon atoms of the fresh and stripped catalyst of Example 3.

DETAILED DESCRIPTION OF THE INVENTION

Preferably the at least partially deactivated (spent) acetylene hydrogenation catalyst is hydrogen stripped with a mixture of hydrogen and inert gas. When pure hydrogen is not used, the hydrogen concentration in such mixtures may be from 0.1 to less than 100%, preferably from 5 to 10%. Since a stripping gas having only 5-10% of hydrogen may be used during the stripping process, any low value hydrogen source, preferably without carbon monoxide, can be employed. For example, hydrogen may be purchased and mixed fresh with an inert gas, or the hydrogen may come from another refining operation. For example, the overhead effluent from a demethanizer, which contains about 5% H_2 in CH_4 (normally used as fuel gas) may be one potential source for hydrogen. It also may be possible to recycle hydrogen that has already been used to regenerate the catalyst.

The percentage of hydrogen in the gas stripping mixture is not critical to the present invention. In the following examples, a mixture of inert gas and around 9-10% hydrogen was used. Any inert gas may be used in the mixture. The most commonly available and most inexpensive inert gas for use in the invention is nitrogen; therefore, nitrogen is a preferred inert gas for use in the present invention.

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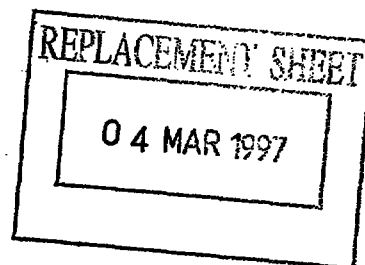
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Although the following examples of the invention describe regeneration of palladium based acetylene reduction catalysts, one of skill in the art will recognize that the hydrogen stripping process of the present invention may be used to regenerate other types of catalysts that are used to hydrogenate acetylene. For example the present process could be used to regenerate acetylene hydrogenation catalysts which contain: Group VIII metals, such as nickel, cobalt, ruthenium, palladium, and platinum; Group VIB metals, such as chromium, molybdenum, and tungsten; or Group IB metals, such as copper, silver, or gold. However, the preferred catalyst for use in the present invention is a catalyst in which the primary active element is palladium, preferably one where palladium comprises approximately 0.01-0.5% by weight of the catalyst, more preferably 0.02-0.05%. A palladium content higher than about 0.5% could deteriorate at the temperatures used in the process of the present invention. Optionally the palladium may be combined with another metal, such as silver.

The catalyst metal is typically carried on a support such as silica or alumina.

The stripping procedure of the invention takes place at a temperature of from 315-400°C (600-750°F), preferably between about 315-372°C (600-700°F), and more preferably at about 350°C (662°F). In order to avoid deactivating the catalyst, especially a palladium based catalyst, or agglomerating the palladium, the temperature of the hydrogen stripping procedure should not exceed about 400°C. The temperature should be at least 315°C to achieve the

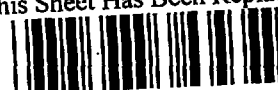


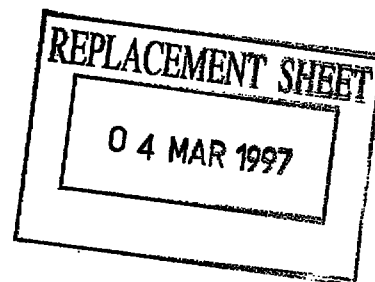


substantially complete regeneration which is commercially desirable, and other process conditions will be readily determinable to enable this objective to be reached.

The pressure at which the stripping takes place may not be critical; however, the stripping preferably takes place between atmospheric pressure (0 psig) and 2.07 MPag (300 psig), and more preferably between atmospheric pressure and 345 kPag (50 psig). Lower cost hydrogen sources having a low content of hydrogen typically are more readily available at lower pressures. In the following examples, pressures of about 2.07 MPag and atmospheric pressure were used. Similarly, the time period required for stripping is not critical, save it should be sufficient to achieve substantially complete regeneration. One of skill in the art will recognize that the amount of time needed for the stripping procedure can be determined by monitoring the amount of hydrocarbon present in the catalyst until a minimum plateau level has been achieved. In the following examples, the stripping time ranged between 16-24 hrs.

The flow rate of the hydrogen through the catalyst should be such that the linear velocity through the catalyst should be at least about 15.2 cm/second (0.5 feet/second). This will ensure uniformity of reactant concentrations and temperatures throughout the reactor during regeneration. It has been found that lower velocities may be insufficient to achieve uniform regeneration of the catalyst. The parameter of linear velocity is used herein rather than, e.g., space velocity because linear velocity





commonly is used to calculate dispersion and mixing phenomena in packed beds. For example, the axial and radial dispersion of reactant concentration are estimated by calculating Peclet numbers (James Carberry, "Chemical and Catalytic Reaction Engineering", p. 162). The linear velocity also is an important factor in controlling heat transfer in the reactor. Furthermore, linear velocities may differ even where the space velocity remains the same. For example, wide and shallow beds will have lower linear velocities than narrow and deep beds will have. However, narrow and deep beds will have a higher pressure drop than wide and shallow beds. Thus, it is desirable to specify either linear velocity or space velocity with the reactor L/D ratio to ensure proper design or scale up of the reactor.

It is a feature of the invention that substantially complete regeneration is achieved without the need for an additional or associated regeneration step, e.g., hydrocarbon wash or steam treat or, particularly, oxygenation. As shown in Example 1 which follows, the process of the invention enables catalyst to be re-used as fresh catalyst after regular hydrogen only regenerations of the catalytic metal sites, preferably in situ in the acetylene reduction reactor. Nevertheless it may be desirable from time to time to clean carbonaceous deposits from the support (as opposed to the catalyst metal) because hydrogen stripping does not remove all of the carbonaceous deposits from the support. Thus it is possible that an air burn may be desirable eventually in order to clean the support to prevent restriction of flow rate, pressure, etc. However, the number of

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air burns that may be employed to clean the supports in such a system will be much less than the frequent air burns that heretofore have been required to regenerate the catalyst. An infrequent air burn to clean the support will be much less intrusive and damaging than the frequent, repetitive air burns required in current catalyst regeneration processes.

The following examples illustrates the invention.

EXAMPLE 1

An aliquot of UCI G58B catalyst ($\text{Pd}/\text{Al}_2\text{O}_3$), deactivated after 200 hours of use as an acetylene hydrogenation catalyst in olefin stream treatment, was stripped with 10% H_2/Ar at linear velocity greater than 15.2 cm/sec and at a temperature which rose from room temperature to about 750°C (1382°F) at a heating rate of about 13 degrees C/min ($23.4^\circ\text{F}/\text{min}$). The carbonaceous residues on the catalyst were analyzed both before and after hydrogen stripping by temperature programmed oxidation (TPO), which detected carbon oxide emission during the TPO burn while the reactor temperature was linearly increased. The TPO spectra of the spent catalyst before and after hydrogen stripping were plotted as Figure 1(a) and (b), respectively.

Before hydrogen stripping, two types of carbonaceous residues were present on the catalyst. A peak at about 400°C (750°F) represents carbonaceous residues that were present on and/or near palladium. A peak at about 510°C (950°F) represents carbonaceous residues that were present on the support. After hydrogen stripping, only one peak appeared at 550°C

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(1022°F). The presence of only this single peak after hydrogen stripping indicated that the carbonaceous residues that were on and/or near the palladium were removed by the hydrogen stripping. Since acetylene conversion occurs mainly on palladium sites in the catalyst, the removal of carbonaceous residues from the palladium can re-expose the palladium active sites and recover substantially all the activity of the palladium. The hydrocarbons that are stripped off the catalyst can be either recycled to the cracker or used as fuel gas.

EXAMPLE 2

A BASF HO11 catalyst (Pd/SiO_2) was subjected for 200 hours to the reaction conditions of 1.5% wt C_2H_2 (in an olefinic stream), 1.6 $\text{H}_2/\text{C}_2\text{H}_2$ molar ratio, 4000 gas hourly space velocity (GHSV), 2.07 MPag (300 psig), and about 66°C (151°F) average bed temperature. After 200 hours, the acetylene conversion of the catalyst decreased from 79% to 58%. The spent catalyst was then regenerated by hydrogen stripping for 16 hours with 5% H_2/N_2 at 2.07 MPag (300 psig) and greater than 15.2 cm/sec linear velocity in the reactor, and about 350°C (662°F). After the hydrogen stripping, the acetylene conversion of the catalyst was 78%. A comparison of the catalyst activity before and after hydrogen stripping is plotted in Figure 2. The results indicate that the hydrogen stripping at about 350°C (662°F) substantially fully regenerated the catalyst.

The temperature used during hydrogen stripping is preferably not too high or else the palladium will begin to agglomerate and will not achieve

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substantially complete regeneration using only a hydrogen treat step. For example, when the catalyst was further hydrogen stripped at about 420°C (788°F) for 16 hours, under otherwise the same conditions, the activity of the catalyst was reduced to 62% acetylene conversion -- a dramatic decrease in catalyst activity.

EXAMPLE 3

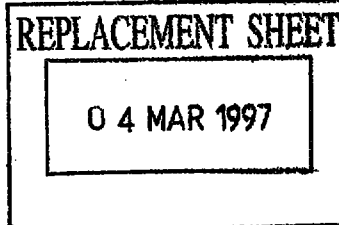
A spent UCI G58E catalyst (Pd/Ag/Al₂O₃) which had been used for acetylene hydrogenation in an ethylene stream was hydrogen stripped at about 350°C (662°F) and 1 atmosphere pressure with 9% H₂/N₂ at linear velocity in the reactor of greater than 15.2 cm/sec, for 24 hours. The performance of the hydrogen stripped catalyst was then compared to the performance of fresh catalyst at 70 hours into the activity test. The results are tabulated in Table I. The parameters of the activity test carried out in a normal hydrogenation reactor were 1.4% wt C₂H₂, 1.2 H₂/C₂H₂ molar ratio, 4900 GHSV, 2.07 MPag (300 psig), about 102°C (215°F) sand-bath temperature.

TABLE I

	<u>Fresh</u>	<u>H₂ Stripped</u>
C ₂ H ₂ Conversion	80%	80%
Selectivity to C ₂ H ₄	57%	67%
Selectivity to C ₂ H ₆	32%	23%
Selectivity to C ₄ +	11%	10%
Deactivation Rate	-0.1%/hr	-0.2%/hr

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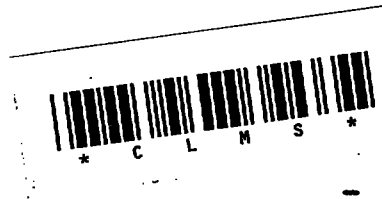
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As seen from Table I, the spent catalyst which had been hydrogen stripped according to the invention unexpectedly had a selectivity to ethylene that was 10 points better than the selectivity of the fresh catalyst. Also, the ethane make was substantially reduced after hydrogen stripping. This result suggests that a "de-edging" process may have occurred which reduced the number of palladium sites responsible for over hydrogenating acetylene/ethylene to ethane.

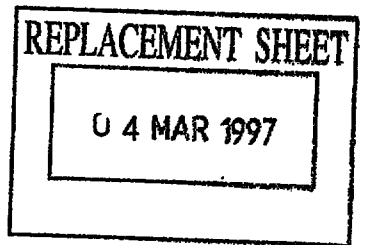
Although the deactivation rate was higher for the hydrogen stripped catalyst, the deactivation rate can be overcome by more frequent hydrogen stripping. Even if more frequent hydrogen stripping is required to regenerate catalyst, the present process may be less time consuming and less damaging to the catalyst than frequent air burns or other additional treatment steps.

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CLAIMS:

1. A method of substantially completely regenerating a catalyst that has been used to remove acetylenic impurities from an olefin stream and which has become at least partially deactivated by that use, which comprises substantially stripping the deactivated catalyst of carbonaceous deposits using hydrogen at a linear velocity of at least 15.2 cm/second (0.5 feet per second), at a temperature of from 315 - 400°C (599 - 750°F) and at other conditions such that substantially complete regeneration is effected, wherein said stripping is essentially the only regeneration treatment employed and occurs in the absence of an oxygenation step.

2. The method of claim 1 wherein the temperature is from 315 - 372°C (600 - 700°F), preferably about 350°C (662°F).

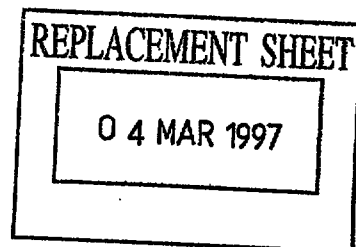
3. The method of claim 1 or 2 wherein the hydrogen stripping employs a gas comprising an inert gas, preferably nitrogen, and from 5 to 10% of hydrogen.

4. The method of any preceding claim wherein the catalyst comprises palladium, optionally together with another metal.

5. The method of claim 4 wherein the palladium comprises from 0.01 to 0.5 wt%, preferably from 0.02 to 0.05% of the catalyst.

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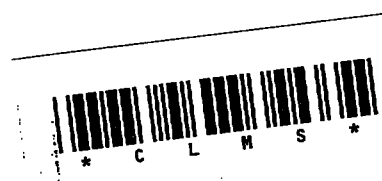




6. The method of any preceding claim wherein the catalyst has been used to remove acetylenic impurities from ethylene.

7. The method of claim 6 wherein after regeneration the catalyst is used to remove acetylenic impurities from ethylene and the selectivity of the catalyst to ethylene is enhanced.

8. The method of any preceding claim wherein the catalyst comprises a silica or alumina support.



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REGENERATION OF ACETYLENE CONVERTER CATALYSTS
BY HYDROGEN STRIPPING

ABSTRACT

An improved method for regenerating acetylene hydrogenation catalysts, particularly palladium based catalysts which have been used to remove acetylenic contaminants from ethylene, which method does not require an oxygenation or other pretreatment step, comprises stripping the spent catalyst with hydrogen at 315-400 °C and a linear hydrogen-containing gas velocity of at least 15.2 cm/second, to achieve substantially complete regeneration.

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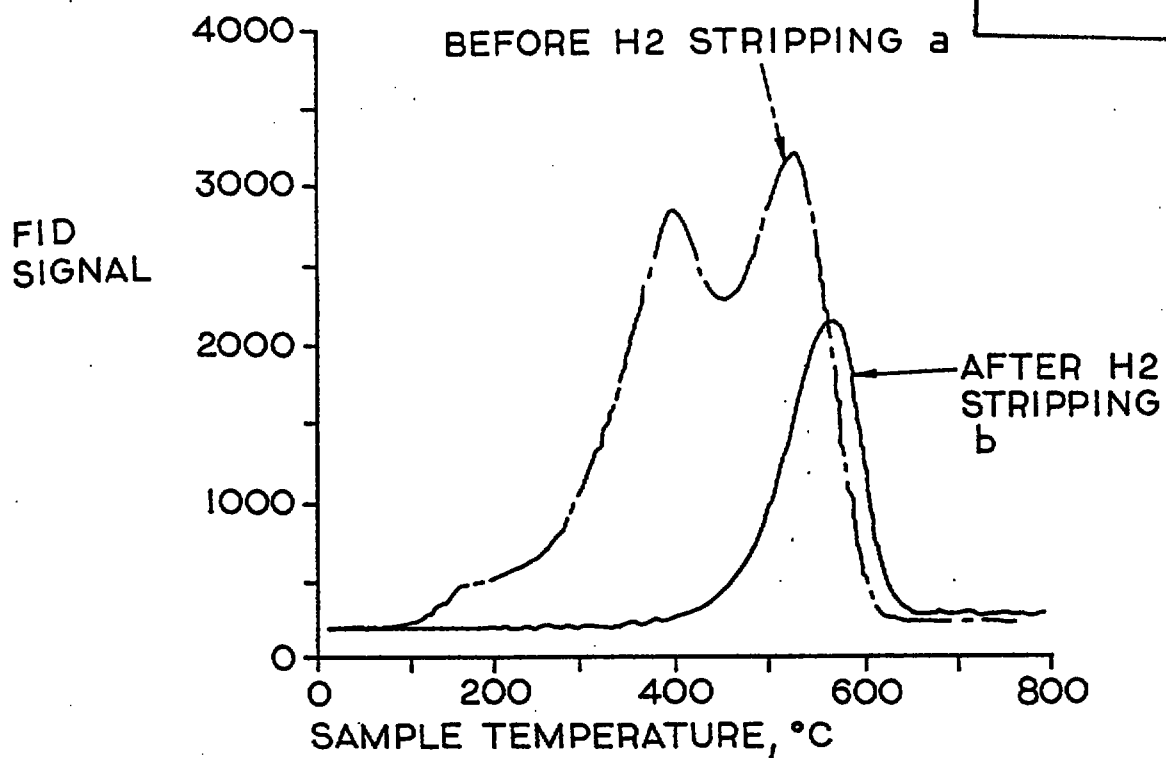


FIG.1

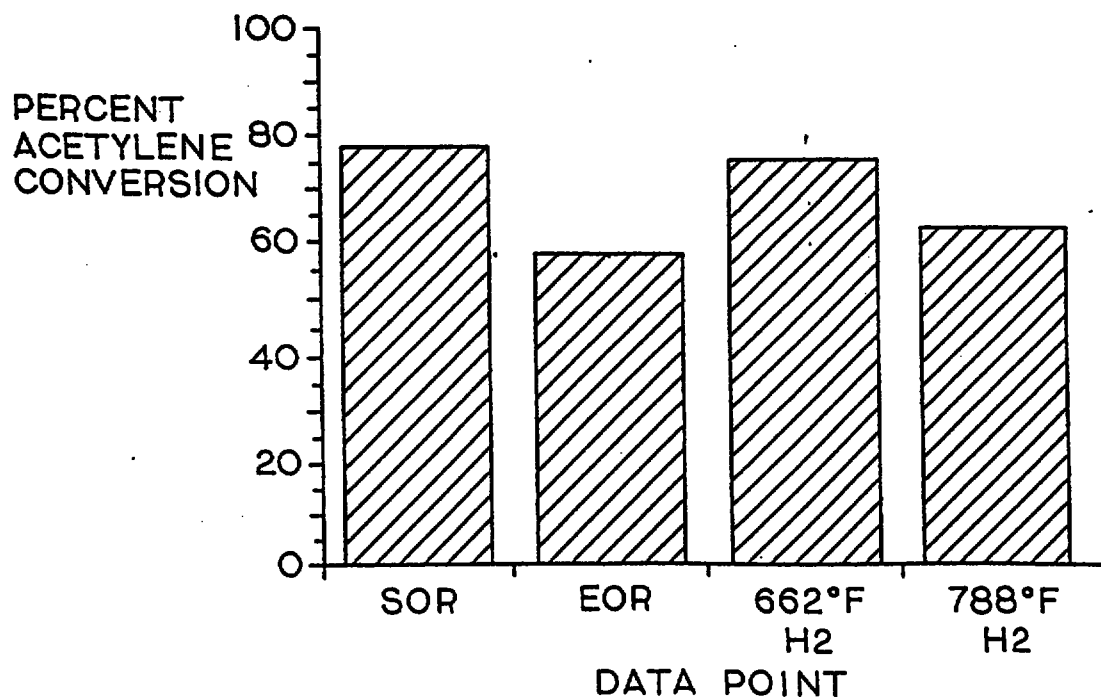


FIG.2

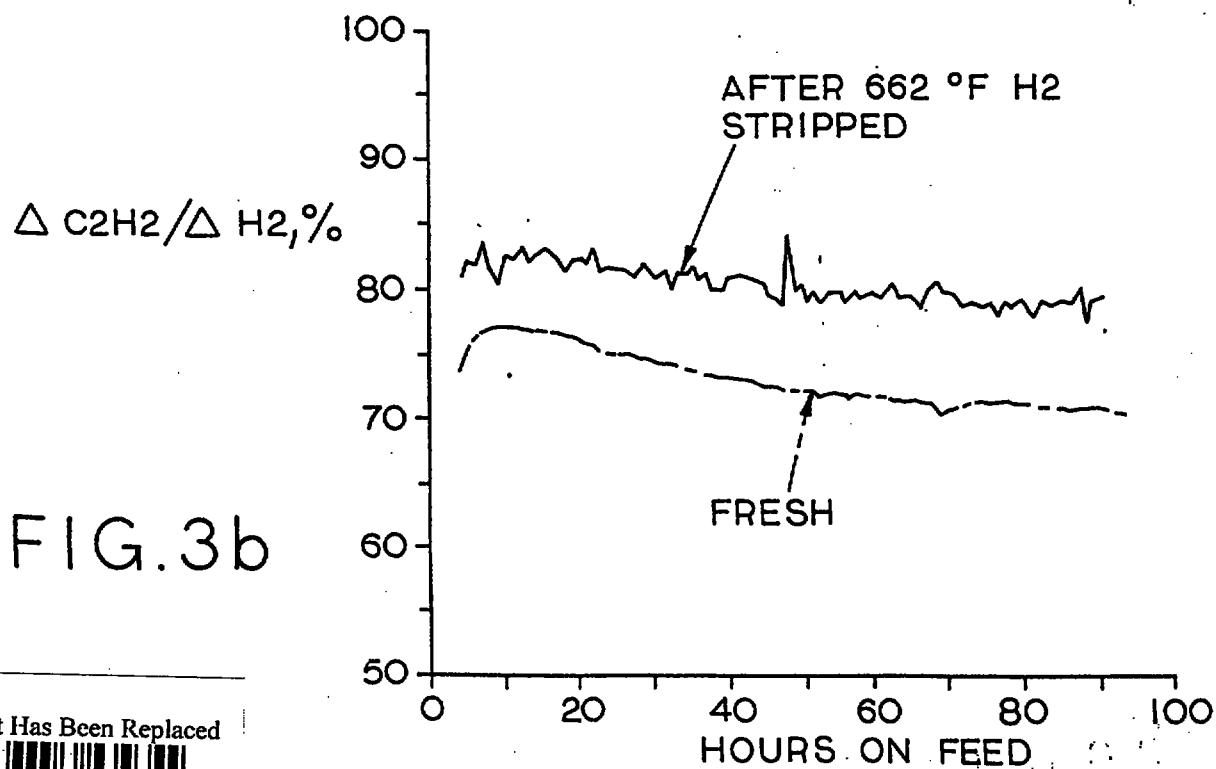
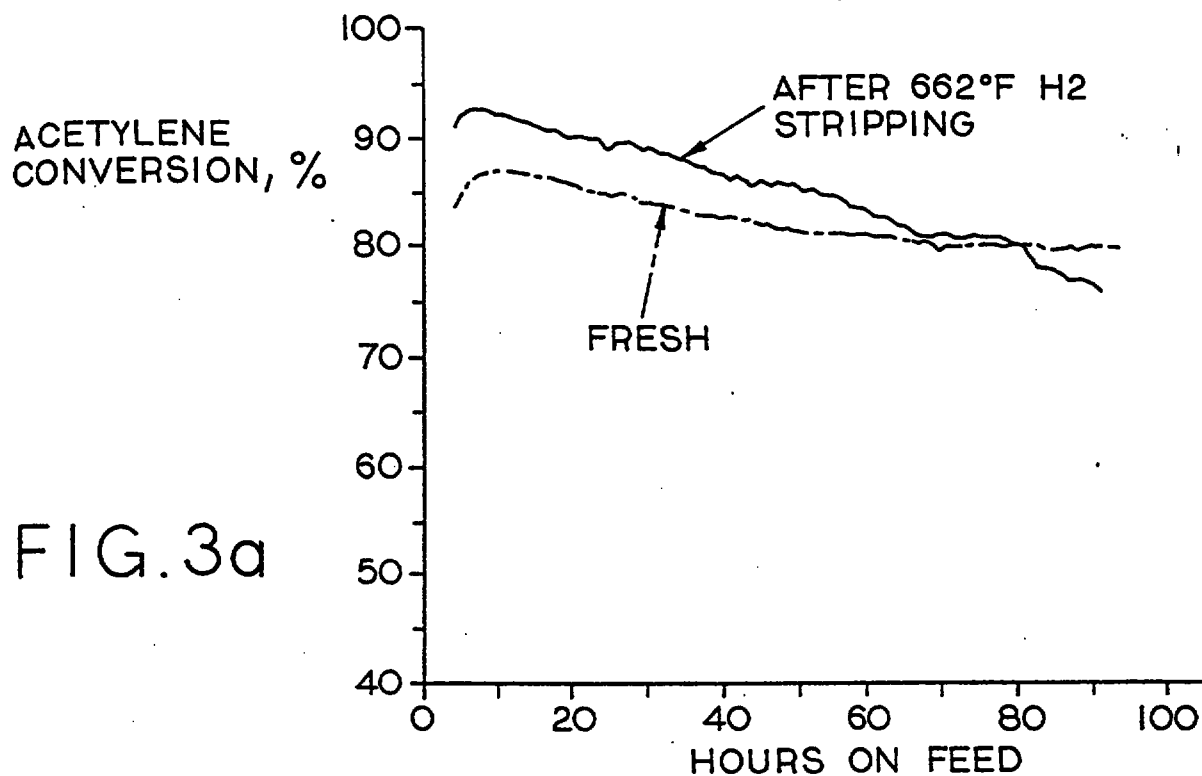
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UCI G58E
1.2 H₂/C₂H₂, 1.4 % C₂H₂,
4900 GHSV, 300 PSI, 215 °F



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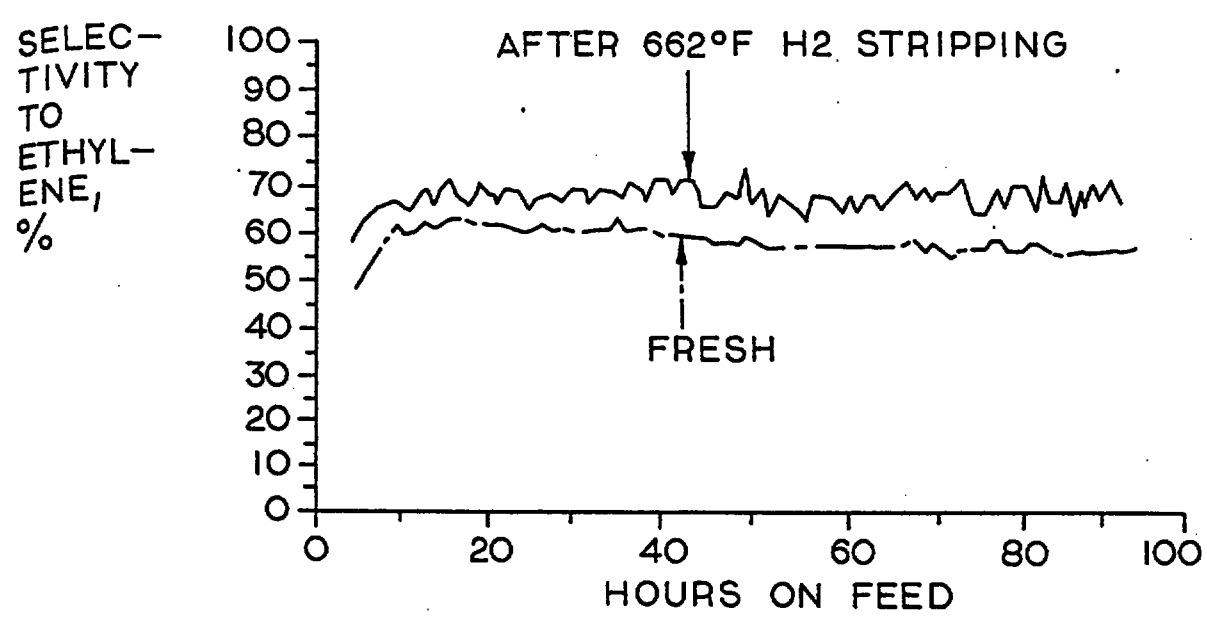


FIG.3c

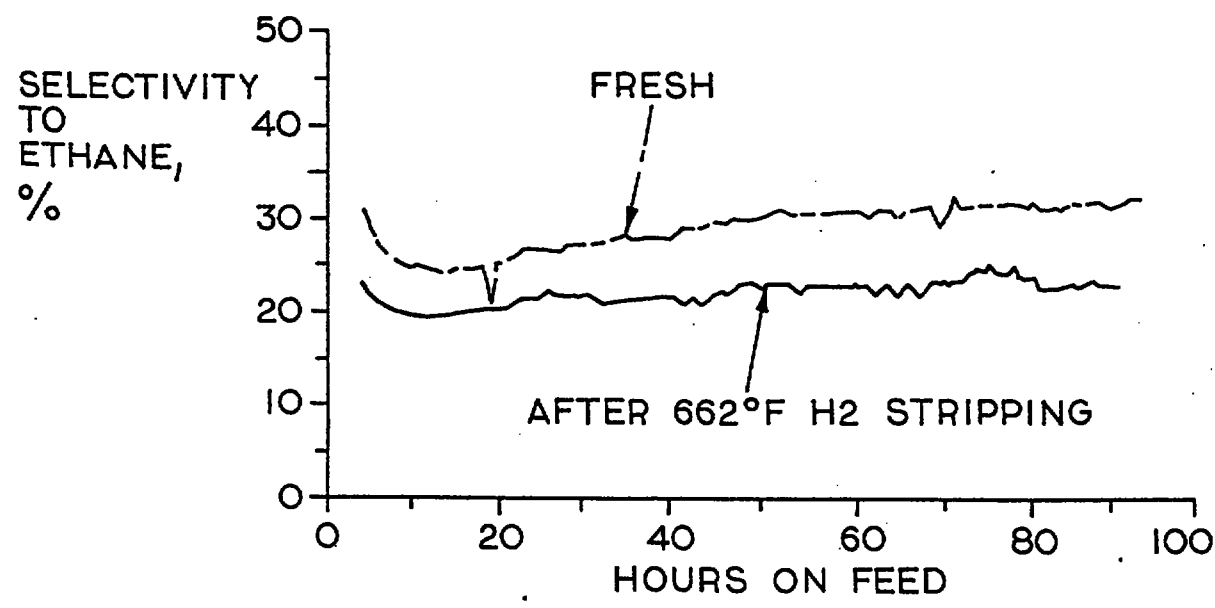


FIG.3d

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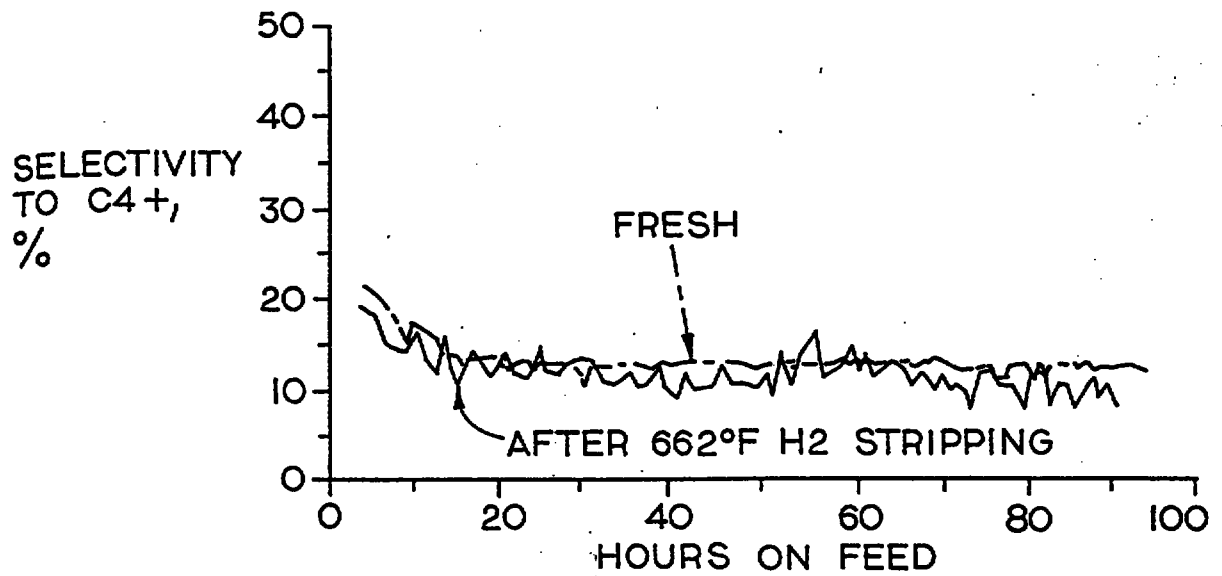
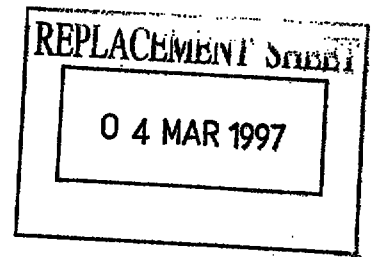
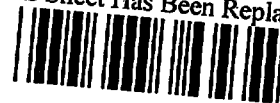


FIG. 3e

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REGENERATION OF ACETYLENE CONVERTER
CATALYSTS BY HYDROGEN STRIPPING

Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an improved method for regenerating catalysts that have been used to remove acetylenic contaminants from olefin product streams. More particularly, the present invention relates to an improved method for regenerating palladium-containing catalysts that have been used to remove acetylenic contaminants from ethylene.

Product streams of liquid or liquefiable olefins and diolefins typically are contaminated with small amounts of acetylenic impurities. For example, the ethylene/ethane fraction in an ethylene plant typically contains 0.5 - 2.0% acetylenic impurities. Such acetylenic contamination is undesirable because acetylene tends to poison the catalysts that are used to convert ethylene to polyethylene. Acetylene also can form metal acetylides which are explosive and which may contaminate the equipment that is used to process such product streams.

It is known that acetylenic impurities can be selectively hydrogenated and thereby removed from such a product stream by passing the product stream over a catalyst (an "acetylene hydrogenation catalyst") in the presence of hydrogen; however, the hydrogenation process typically results in the deposition of a green oil on the catalyst which deactivates the catalyst. Therefore, acetylene hydrogenation processes typically include an oxygenation step or a "burn" step to remove the deactivating carbonaceous residues from the catalyst followed by a hydrogen reduction step to reactivate the catalyst. See, e.g., US-A-3,812,057 (Morgan) and US-A-4,424,255 (Toyoda).

An oxygenation step followed by hydrogen reduction normally is effective to regenerate an acetylene hydrogenation catalyst; however, there are many disadvantages to the use of an oxygenation step during regeneration of such catalysts.

First, when oxygen and hydrogen come together under the conditions used to regenerate the catalyst, an exothermic reaction is produced which may result in uncontrolled temperature runaway. Thus, before the regeneration is performed, it is necessary to purge the catalyst of hydrogen and hydrocarbons using an inert gas, such as nitrogen gas, both before and after the oxygen-containing stream is introduced. The purging process is both tedious and time consuming. Furthermore, if the regeneration is performed in situ, the concentration of oxygen in the regeneration gas stream must be regulated carefully in order to avoid reactor temperature run-away. It would be advantageous if acetylene hydrogenation catalysts could be regenerated using a method which did not require such time consuming purging and monitoring.

The use of an oxygenation step during regeneration of an acetylene hydrogenation catalyst also presents an environmental concern due to the resulting emission of carbon monoxide, carbon dioxide, and unburned hydrocarbons. The hydrocarbon residue that remains on the catalyst can comprise up to 10 wt% of the catalyst. The oxygenation of this amount of residue results in the emission of a substantial amount of carbon monoxide and carbon dioxide. In addition, the emission during oxygenation may contain approximately 6-10% of unburned hydrocarbons. It would be advantageous if acetylene reduction catalysts could be regenerated in a manner that did not result in such environmentally undesirable emissions.

Regeneration of acetylene hydrogenation catalysts using an oxygenation step also is undesirable because the oxygenation step has a negative impact on the life of

the catalyst. A catalyst that has been used to hydrogenate acetylene typically must be regenerated once every one to three months. Acetylene hydrogenation catalysts are heat sensitive, and exposure to excessive heat decreases the activity of the catalyst. The oxygenation step that is used in most regeneration processes typically is run at temperatures between 371-455°C (700-850°F). The exposure of an acetylene hydrogenation catalyst to such high temperatures at such regular intervals takes a great toll on the life of the catalyst. It would be advantageous if the regeneration of such catalysts could take place at lower temperatures which reduced the thermal stress induced during the regeneration.

Some of these disadvantages can be avoided if the catalyst is regenerated ex situ, or outside of the reactor. However, the unloading and reloading of the reactor with the catalyst is a time consuming process. Even if the regeneration process is performed ex situ, the catalyst still must be purged with an inert gas both before unloading and after reloading the reactor. Thus, regardless of where the regeneration process takes place, significant reactor down time is required if the catalyst is regenerated using a process that includes an oxidation step.

For all of these reasons, it would be advantageous if acetylene reducing catalysts could be regenerated without an oxygenation step. Col. 4, lines 16-35 of US-A-3,912,789 acknowledges that partial regeneration can be accomplished using a hydrogenation step alone. However, this patent teaches that full regeneration of an exhausted catalyst requires an oxygenation step. Therefore, a process has yet to be developed that can fully regenerate acetylene reduction catalysts without the need for an oxygenation step.

Not only is an oxygenation step undesirable, but any additional step in the regeneration procedure is undesirable because each step requires a change of conditions and switch over techniques which can be del-

eterious to the performance or longevity of the regenerated catalyst. For example, GB-1,158,418 teaches a method of regenerating hydrogenation catalysts comprising a hydrocarbon wash step followed by a hydrogen treatment. Indeed this patent discusses an already known method consisting of contacting hydrogen with the catalyst at an elevated temperature (p. 1, line 77 - p. 2, line 10), but reports that this known method was still insufficient to restore completely the initial activity of the selective hydrogenation catalyst.

US-A-2,946,829 discloses a process of making a Pd/Al₂O₃ catalyst for selective hydrogenation, used with the industry standard method of regeneration, which uses steam to provide heat to attain the needed temperature to burn the polymeric deposits off the catalyst. When a small amount of air is mixed into the steam (see Example 3, col. 5, l. 52-55), the resulting catalyst is relatively free of carbonaceous deposits. The main function of the hydrogen reduction step is to reduce the oxidized metal back to its metallic state. In fact, the hydrogen reduction step is not even required, as shown in Example 3, col. 5, l. 65. On day 17, regeneration 8 did not include a reduction step. The catalyst nevertheless was put back on stream after steam treatment and exhibited very high activity, i.e., at a space velocity of 2,000 and 66°C (150°F), acetylene in the reactor outlet dropped from an inlet concentration of 0.35% to 1.3 ppm. This compares favorably to the results of the first regeneration, Example 1, which did use a hydrogen reduction step after steam treatment -- 5 ppm acetylene at the reactor outlet at a much lower space velocity of 1,000 and 54°C (130°F).

In addition, US-A-2,946,829 teaches the need for vigorous regeneration in order to remove polymer deposits. Such severe regeneration leads to a loss of physical strength, in the hydrogenation catalyst, or to impaired activity or selectivity (col. 2, lines 30-37). The vigorous step in the disclosure is the step of burning off

the polymer deposits in the presence of steam -- not the hydrogen reduction step. Thus, this art teaches that the steam treatment step is essential to regeneration of a hydrogenation catalyst.

GB-A-907,348 teaches the partial regeneration of a nickel catalyst using a hydrogen treatment. Although a temperature range of 200-600°C is mentioned, all of the actual regenerations described are carried out at temperatures in the range of 204-250°C. In the Provisional Specification of GB-A-907,348, temperatures at the lower end of the range are said to be preferred, particularly 200-300°C. From the actual experiments of GB-A-907,348, regeneration at 250°C did not cause recovery of fresh catalyst activity, and the stability of the regenerated catalyst was lower except in the experiment that used the lowest temperature (204°C). (See Examples 1-3.) The failure to recover the activity of fresh catalyst is clear because a higher temperature is required to maintain the same hydrogen consumption during regeneration (Example 1, 127°C fresh v. 143°C regenerated; Example 2, 127°C fresh v. 138°C regenerated). And, in Examples 1 and 2 (which used a regeneration temperature of 250°C), the stability of the regenerated catalyst is lower (Example 1, fresh catalyst required 152°C after 670 hours v. regenerated catalyst required 166°C after 477 hours; Example 2, fresh catalyst required 127°C after 335 hours v. regenerated catalyst required 138°C after 127 hours). However, in Example 3 (which regenerates the catalyst at a temperature of 204°C), although the activity of the fresh catalyst is not completely recovered, the stability of the regenerated catalyst is higher than the stability of the fresh catalyst (regenerated catalyst required 142°C after 1410 hours, fresh catalyst required 160°C after 327 hours). Thus this publication teaches away from the regeneration of catalysts using hydrogen at temperatures that are above 250°C.

SUMMARY OF THE INVENTION

According to the present invention there is provided a method of substantially completely regenerating a catalyst that has been used to remove acetylenic impurities from an olefin stream and which has become at least partially deactivated by that use, which comprises substantially stripping the deactivated catalyst of carbonaceous deposits using hydrogen at a linear velocity of at least 15.2 cm/second (0.5 feet per second), at a temperature of from 315 - 400°C (599 - 750°F) and at other conditions such that substantially complete regeneration is effected, wherein said stripping is essentially the only regeneration treatment employed and occurs in the absence of an oxygenation step.

It is a feature of the invention that acetylene reduction catalysts can be substantially fully regenerated by hydrogen stripping, alone, at relatively low temperatures which are nevertheless greater than those taught away from in prior art such as GB-A-907,348. It has also been found that palladium-containing catalysts that have been used to purify ethylene unexpectedly have a better selectivity to ethylene after they are hydrogen stripped according to the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a chart showing the Temperature Programmed Oxidation (TPO) spectra of the UCI G58B catalyst of Example 1 before (a) and after (b) hydrogen stripping.

Fig. 2 is a bar graph comparing the catalyst activity of the BASF H011 catalyst of Example 2 before and after hydrogen stripping. "SOR" under the first bar in the graph stands for activity at the start of the run. "EOR" under the second bar in the graph stands for activity at the end of the run. The bar above "662°F H₂" represents the activity of the substantially completely regenerated catalyst after hydrogen stripping according to the

invention at about 350°C (662°F). The bar above "788°F H₂" represents the (reduced) activity of the incompletely regenerated catalyst after further hydrogen stripping outside the scope of the invention at about 420°C (788°F).

Fig. 3(a) is a graph comparing the acetylene conversion activity of the UCI G58E catalyst of Example 3 when fresh to the activity of that same (substantially completely regenerated) catalyst after it has been hydrogen stripped according to the present invention at about 350°C (662°F).

Fig. 3(b) is a graph comparing the deactivation rate of the fresh and stripped catalyst of Example 3.

Fig. 3(c) is a graph comparing the selectivity to ethylene of the fresh and stripped catalyst of Example 3.

Fig. 3(d) is a graph comparing the selectivity to ethane of the fresh and stripped catalyst of Example 3.

Fig. 3(e) is a graph comparing the selectivity to hydrocarbons having four or more carbon atoms of the fresh and stripped catalyst of Example 3.

DETAILED DESCRIPTION OF THE INVENTION

Preferably the at least partially deactivated (spent) acetylene hydrogenation catalyst is hydrogen stripped with a mixture of hydrogen and inert gas. When pure hydrogen is not used, the hydrogen concentration in such mixtures may be from 0.1 to less than 100%, preferably from 5 to 10%. Since a stripping gas having only 5-10% of hydrogen may be used during the stripping process, any low value hydrogen source, preferably without carbon monoxide, can be employed. For example, hydrogen may be purchased and mixed fresh with an inert gas, or the hydrogen may come from another refining operation. For example, the overhead effluent from a demethanizer, which contains about 5% H₂ in CH₄ (normally used as fuel gas) may be one potential source for hydrogen. It also may be possible to recycle hydrogen that has already been used to regenerate the catalyst.

The percentage of hydrogen in the gas stripping mixture is not critical to the present invention. In the following examples, a mixture of inert gas and around 9-10% hydrogen was used. Any inert gas may be used in the mixture. The most commonly available and most inexpensive inert gas for use in the invention is nitrogen; therefore, nitrogen is a preferred inert gas for use in the present invention.

Although the following examples of the invention describe regeneration of palladium based acetylene reduction catalysts, one of skill in the art will recognize that the hydrogen stripping process of the present invention may be used to regenerate other types of catalysts that are used to hydrogenate acetylene. For example the present process could be used to regenerate acetylene hydrogenation catalysts which contain: Group VIII metals, such as nickel, cobalt, ruthenium, palladium, and platinum; Group VIB metals, such as chromium, molybdenum, and tungsten; or Group IB metals, such as copper, silver, or gold. However, the preferred catalyst for use in the present invention is a catalyst in which the primary active element is palladium, preferably one where palladium comprises approximately 0.01-0.5% by weight of the catalyst, more preferably 0.02-0.05%. A palladium content higher than about 0.5% could deteriorate at the temperatures used in the process of the present invention. Optionally the palladium may be combined with another metal, such as silver.

The catalyst metal is typically carried on a support such as silica or alumina.

The stripping procedure of the invention takes place at a temperature of from 315-400°C (600-750°F), preferably between about 315-372°C (600-700°F), and more preferably at about 350°C (662°F). In order to avoid deactivating the catalyst, especially a palladium based catalyst, or agglomerating the palladium, the temperature of the hydrogen stripping procedure should not exceed about 400°C. The temperature should be at

least 315°C to achieve the substantially complete regeneration which is commercially desirable, and other process conditions will be readily determinable to enable this objective to be reached.

The pressure at which the stripping takes place may not be critical; however, the stripping preferably takes place between atmospheric pressure (0 psig) and 2.07 MPag (300 psig), and more preferably between atmospheric pressure and 345 kPag (50 psig). Lower cost hydrogen sources having a low content of hydrogen typically are more readily available at lower pressures. In the following examples, pressures of about 2.07 MPag and atmospheric pressure were used. Similarly, the time period required for stripping is not critical, save it should be sufficient to achieve substantially complete regeneration. One of skill in the art will recognize that the amount of time needed for the stripping procedure can be determined by monitoring the amount of hydrocarbon present in the catalyst until a minimum plateau level has been achieved. In the following examples, the stripping time ranged between 16-24 hrs.

The flow rate of the hydrogen through the catalyst should be such that the linear velocity through the catalyst should be at least about 15.2 cm/second (0.5 feet/second). This will ensure uniformity of reactant concentrations and temperatures throughout the reactor during regeneration. It has been found that lower velocities may be insufficient to achieve uniform regeneration of the catalyst. The parameter of linear velocity is used herein rather than, e.g., space velocity because linear velocity commonly is used to calculate dispersion and mixing phenomena in packed beds. For example, the axial and radial dispersion of reactant concentration are estimated by calculating Peclet numbers (James Carberry, "Chemical and Catalytic Reaction Engineering", p. 162). The linear velocity also is an important factor in controlling heat transfer in the reactor. Furthermore, linear velocities may differ even where the space velocity remains the same. For example, wide and shallow beds will have lower linear velocities than narrow and deep

beds will have. However, narrow and deep beds will have a higher pressure drop than wide and shallow beds. Thus, it is desirable to specify either linear velocity or space velocity with the reactor L/D ratio to ensure proper design or scale up of the reactor.

It is a feature of the invention that substantially complete regeneration is achieved without the need for an additional or associated regeneration step, e.g., hydrocarbon wash or steam treat or, particularly, oxygenation. As shown in Example 1 which follows, the process of the invention enables catalyst to be re-used as fresh catalyst after regular hydrogen only regenerations of the catalytic metal sites, preferably in situ in the acetylene reduction reactor. Nevertheless it may be desirable from time to time to clean carbonaceous deposits from the support (as opposed to the catalyst metal) because hydrogen stripping does not remove all of the carbonaceous deposits from the support. Thus it is possible that an air burn may be desirable eventually in order to clean the support to prevent restriction of flow rate, pressure, etc. However, the number of air burns that may be employed to clean the supports in such a system will be much less than the frequent air burns that heretofore have been required to regenerate the catalyst. An infrequent air burn to clean the support will be much less intrusive and damaging than the frequent, repetitive air burns required in current catalyst regeneration processes.

The following examples illustrates the invention.

EXAMPLE 1

An aliquot of UCI G58B catalyst ($\text{Pd}/\text{Al}_2\text{O}_3$), deactivated after 200 hours of use as an acetylene hydrogenation catalyst in olefin stream treatment, was stripped with 10% H_2/Ar at linear velocity greater than 15.2 cm/sec and at a temperature which rose from room temperature to about 750°C (1382°F) at a heating rate of about 13 degrees C/min ($23.4^\circ\text{F}/\text{min}$). The carbona-

aceous residues on the catalyst were analyzed both before and after hydrogen stripping by temperature programmed oxidation (TPO), which detected carbon oxide emission during the TPO burn while the reactor temperature was linearly increased. The TPO spectra of the spent catalyst before and after hydrogen stripping were plotted as Figure 1(a) and (b), respectively.

Before hydrogen stripping, two types of carbonaceous residues were present on the catalyst. A peak at about 400°C (750°F) represents carbonaceous residues that were present on and/or near palladium. A peak at about 510°C (950°F) represents carbonaceous residues that were present on the support. After hydrogen stripping, only one peak appeared at 550°C (1022°F). The presence of only this single peak after hydrogen stripping indicated that the carbonaceous residues that were on and/or near the palladium were removed by the hydrogen stripping. Since acetylene conversion occurs mainly on palladium sites in the catalyst, the removal of carbonaceous residues from the palladium can re-expose the palladium active sites and recover substantially all the activity of the palladium. The hydrocarbons that are stripped off the catalyst can be either recycled to the cracker or used as fuel gas.

EXAMPLE 2

A BASF HO11 catalyst (Pd/SiO₂) was subjected for 200 hours to the reaction conditions of 1.5% wt C₂H₂ (in an olefinic stream), 1.6 H₂/C₂H₂ molar ratio, 4000 gas hourly space velocity (GHSV), 2.07 MPag (300 psig), and about 66°C (151°F) average bed temperature. After 200 hours, the acetylene conversion of the catalyst decreased from 79% to 58%. The spent catalyst was then regenerated by hydrogen stripping for 16 hours with 5% H₂/N₂ at 2.07 MPag (300 psig) and greater than 15.2 cm/sec linear velocity in the reactor, and about 350°C (662°F). After the hydrogen stripping, the acetylene conversion of the catalyst was 78%. A comparison

of the catalyst activity before and after hydrogen stripping is plotted in Figure 2. The results indicate that the hydrogen stripping at about 350°C (662°F) substantially fully regenerated the catalyst.

The temperature used during hydrogen stripping is preferably not too high or else the palladium will begin to agglomerate and will not achieve substantially complete regeneration using only a hydrogen treat step. For example, when the catalyst was further hydrogen stripped at about 420°C (788°F) for 16 hours, under otherwise the same conditions, the activity of the catalyst was reduced to 62% acetylene conversion -- a dramatic decrease in catalyst activity.

EXAMPLE 3

A spent UCI G58E catalyst (Pd/Ag/Al₂O₃) which had been used for acetylene hydrogenation in an ethylene stream was hydrogen stripped at about 350°C (662°F) and 1 atmosphere pressure with 9% H₂/N₂ at linear velocity in the reactor of greater than 15.2 cm/sec, for 24 hours. The performance of the hydrogen stripped catalyst was then compared to the performance of fresh catalyst at 70 hours into the activity test. The results are tabulated in Table I. The parameters of the activity test carried out in a normal hydrogenation reactor were 1.4% wt C₂H₂, 1.2 H₂/C₂H₂ molar ratio, 4900 GHSV, 2.07 MPag (300 psig), about 102°C (215°F) sand-bath temperature.

TABLE I

	Fresh	H ₂ Stripped
C ₂ H ₂ Conversion	80%	80%
Selectivity to C ₂ H ₄	57%	67%
Selectivity to C ₂ H ₆	32%	23%
Selectivity to C ₄ +	11%	10%
Deactivation Rate	-0.1%/hr	-0.2%/hr

As seen from Table I, the spent catalyst which had been hydrogen stripped according to the invention unexpectedly had a selectivity to ethylene that was 10 points better than the selectivity of the fresh catalyst. Also, the ethane make was substantially reduced after hydrogen stripping. This result suggests that a "de-edging" process may have occurred which reduced the number of palladium sites responsible for over hydrogenating acetylene/ethylene to ethane.

Although the deactivation rate was higher for the hydrogen stripped catalyst, the deactivation rate can be overcome by more frequent hydrogen stripping. Even if more frequent hydrogen stripping is required to regenerate catalyst, the present process may be less time consuming and less damaging to the catalyst than frequent air burns or other additional treatment steps.

Claims

1. A method of substantially completely regenerating a catalyst that has been used to remove acetylenic impurities from an olefin stream and which has become at least partially deactivated by that use, which comprises substantially stripping the deactivated catalyst of carbonaceous deposits using hydrogen at a linear velocity of at least 15.2 cm/second (0.5 feet per second), at a temperature of from 315 - 400°C (599 - 750°F) and at other conditions such that substantially complete regeneration is effected, wherein said stripping is essentially the only regeneration treatment employed and occurs in the absence of an oxygenation step.
2. The method of claim 1 wherein the temperature is from 315 - 372°C (600 - 700°F), preferably about 350°C (662°F).
3. The method of claim 1 or 2 wherein the hydrogen stripping employs a gas comprising an inert gas, preferably nitrogen, and from 5 to 10% of hydrogen.
4. The method of any preceding claim wherein the catalyst comprises palladium, optionally together with another metal.
5. The method of claim 4 wherein the palladium comprises from 0.01 to 0.5 wt%, preferably from 0.02 to 0.05% of the catalyst.
6. The method of any preceding claim wherein the catalyst has been used to remove acetylenic impurities from ethylene.

7. The method of claim 6 wherein after regeneration the catalyst is used to remove acetylenic impurities from ethylene and the selectivity of the catalyst to ethylene is enhanced.
8. The method of any preceding claim wherein the catalyst comprises a silica or alumina support.

REGENERATION OF ACETYLENE CONVERTER CATALYSTS
BY HYDROGEN STRIPPING

ABSTRACT

An improved method for regenerating acetylene hydrogenation catalysts, particularly palladium based catalysts which have been used to remove acetylenic contaminants from ethylene, which method does not require an oxygenation or other pretreatment step, comprises stripping the spent catalyst with hydrogen at 315-400 °C and a linear hydrogen containing gas velocity of at least 15.2 cm/second, to achieve substantially complete regeneration.

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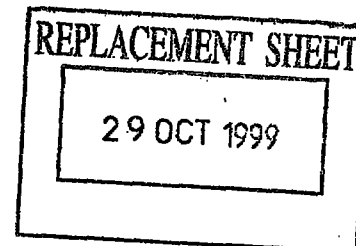
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REGENERATION OF ACETYLENE CONVERTER
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BACKGROUND OF THE INVENTION

Field of the invention



The present invention relates to an improved method for regenerating catalysts that have been used to remove acetylenic contaminants from olefin product streams. More particularly, the present invention relates to an improved method for regenerating palladium-containing catalysts that have been used to remove acetylenic contaminants from ethylene.

Product streams of liquid or liquefiable olefins and diolefins typically are contaminated with small amounts of acetylenic impurities. For example, the ethylene/ethane fraction in an ethylene plant typically contains 0.5 - 2.0% acetylenic impurities. Such acetylenic contamination is undesirable because acetylene tends to poison the catalysts that are used to convert ethylene to polyethylene. Acetylene also can form metal acetylides which are explosive and which may contaminate the equipment that is used to process such product streams.

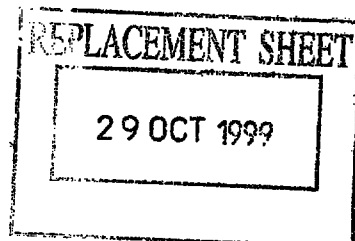
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First, when oxygen and hydrogen come together under the conditions used to regenerate the catalyst, an exothermic reaction is produced which may result in uncontrolled temperature runaway. Thus, before the regeneration is performed, it is necessary to purge the catalyst of hydrogen and hydrocarbons using an inert gas, such as nitrogen gas, both before and after the oxygen-containing stream is introduced. The purging process is both tedious and time consuming. Furthermore, if the regeneration is performed in situ, the concentration of oxygen in the regeneration gas stream must be regulated carefully in order to avoid reactor temperature run-away. It would be advantageous if acetylene hydrogenation catalysts could be regenerated using a method which did not require such time consuming purging and monitoring.

The use of an oxygenation step during regeneration of an acetylene hydrogenation catalyst also presents an environmental concern due to the resulting emission of carbon monoxide, carbon dioxide, and unburned hydrocarbons. The hydrocarbon residue that remains on the catalyst can comprise up to 10 wt% of the catalyst. The oxygenation of this amount of residue results in the emission of a substantial amount of carbon monoxide and carbon dioxide. In addition, the emission during oxygenation may contain approximately 6-10% of unburned hydrocarbons. It would be advantageous if acetylene reduction catalysts could be regenerated in a manner that did not result in such environmentally undesirable emissions.

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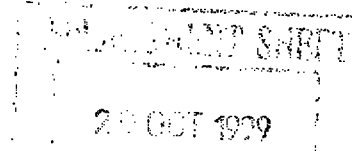


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Some of these disadvantages can be avoided if the catalyst is regenerated ex situ, or outside of the reactor. However, the unloading and reloading of the reactor with the catalyst is a time consuming process. Even if the regeneration process is performed ex situ, the catalyst still must be purged with an inert gas both before unloading and after reloading the reactor. Thus, regardless of where the regeneration process takes place, significant reactor down time is required if the catalyst is regenerated using a process that includes an oxidation step.

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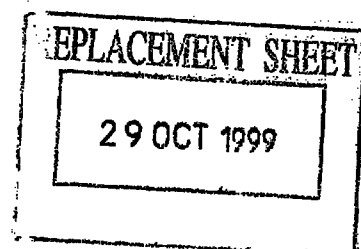
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In addition, US-A-2,946,829 teaches the need for vigorous regeneration in order to remove polymer deposits. Such severe regeneration leads to a loss of physical strength, in the hydrogenation catalyst, or to impaired activity or selectivity (col. 2, lines 30-37). The vigorous step in the disclosure is the step of burning off



the polymer deposits in the presence of steam -- not the hydrogen reduction step. Thus, this art teaches that the steam treatment step is essential to regeneration of a hydrogenation catalyst.

GB-A-907,348 teaches the partial regeneration of a nickel catalyst using a hydrogen treatment. Although a temperature range of 200-600°C is mentioned, all of the actual regenerations described are carried out at temperatures in the range of 204-250°C. In the Provisional Specification of GB-A-907,348, temperatures at the lower end of the range are said to be preferred, particularly 200-300°C. From the actual experiments of GB-A-907,348, regeneration at 250°C did not cause recovery of fresh catalyst activity, and the stability of the regenerated catalyst was lower except in the experiment that used the lowest temperature (204°C). (See Examples 1-3.) The failure to recover the activity of fresh catalyst is clear because a higher temperature is required to maintain the same hydrogen consumption during regeneration (Example 1, 127°C fresh v. 143°C regenerated; Example 2, 127°C fresh v. 138°C regenerated). And, in Examples 1 and 2 (which used a regeneration temperature of 250°C), the stability of the regenerated catalyst is lower (Example 1, fresh catalyst required 152°C after 670 hours v. regenerated catalyst required 166°C after 477 hours; Example 2, fresh catalyst required 127°C after 335 hours v. regenerated catalyst required 138°C after 127 hours). However, in Example 3 (which regenerates the catalyst at a temperature of 204°C), although the activity of the fresh catalyst is not completely recovered, the stability of the regenerated catalyst is higher than the stability of the fresh catalyst (regenerated catalyst required 142°C after 1410 hours, fresh catalyst required 160°C after 327 hours). Thus this publication teaches away from the regeneration of catalysts using hydrogen at temperatures that are above 250°C.

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SUMMARY OF THE INVENTION

According to the present invention there is provided a method of substantially completely regenerating a catalyst that has been used to remove acetylenic impurities from an olefin stream and which has become at least partially deactivated by that use, which comprises substantially stripping the deactivated catalyst of carbonaceous deposits using hydrogen at a linear velocity of at least 15.2 cm/second (0.5 feet per second), at a temperature of from 315 - 400°C (599 - 750°F) and at other conditions such that substantially complete regeneration is effected, wherein said stripping is essentially the only regeneration treatment employed and occurs in the absence of an oxygenation step.

It is a feature of the invention that acetylene reduction catalysts can be substantially fully regenerated by hydrogen stripping, alone, at relatively low temperatures which are nevertheless greater than those taught away from in prior art such as GB-A-907,348. It has also been found that palladium-containing catalysts that have been used to purify ethylene unexpectedly have a better selectivity to ethylene after they are hydrogen stripped according to the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a chart showing the Temperature Programmed Oxidation (TPO) spectra of the UCI G58B catalyst of Example 1 before (a) and after (b) hydrogen stripping.

Fig. 2 is a bar graph comparing the catalyst activity of the BASF H011 catalyst of Example 2 before and after hydrogen stripping. "SOR" under the first bar in the graph stands for activity at the start of the run. "EOR" under the second bar in the graph stands for activity at the end of the run. The bar above "662°F H₂" represents the activity of the substantially completely regenerated catalyst after hydrogen stripping according to the

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invention at about 350°C (662°F). The bar above "788°F H₂" represents the (reduced) activity of the incompletely regenerated catalyst after further hydrogen stripping outside the scope of the invention at about 420°C (788°F).

Fig. 3(a) is a graph comparing the acetylene conversion activity of the UCI G58E catalyst of Example 3 when fresh to the activity of that same (substantially completely regenerated) catalyst after it has been hydrogen stripped according to the present invention at about 350°C (662°F).

Fig. 3(b) is a graph comparing the deactivation rate of the fresh and stripped catalyst of Example 3.

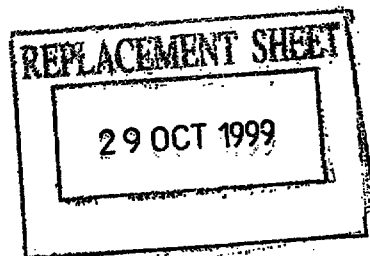
Fig. 3(c) is a graph comparing the selectivity to ethylene of the fresh and stripped catalyst of Example 3.

Fig. 3(d) is a graph comparing the selectivity to ethane of the fresh and stripped catalyst of Example 3.

Fig. 3(e) is a graph comparing the selectivity to hydrocarbons having four or more carbon atoms of the fresh and stripped catalyst of Example 3.

DETAILED DESCRIPTION OF THE INVENTION

Preferably the at least partially deactivated (spent) acetylene hydrogenation catalyst is hydrogen stripped with a mixture of hydrogen and inert gas. When pure hydrogen is not used, the hydrogen concentration in such mixtures may be from 0.1 to less than 100%, preferably from 5 to 10%. Since a stripping gas having only 5-10% of hydrogen may be used during the stripping process, any low value hydrogen source, preferably without carbon monoxide, can be employed. For example, hydrogen may be purchased and mixed fresh with an inert gas, or the hydrogen may come from another refining operation. For example, the overhead effluent from a demethanizer, which contains about 5% H₂ in CH₄ (normally used as fuel gas) may be one potential source for hydrogen. It also may be possible to recycle hydrogen that has already been used to regenerate the catalyst.



The percentage of hydrogen in the gas stripping mixture is not critical to the present invention. In the following examples, a mixture of inert gas and around 9-10% hydrogen was used. Any inert gas may be used in the mixture. The most commonly available and most inexpensive inert gas for use in the invention is nitrogen; therefore, nitrogen is a preferred inert gas for use in the present invention.

Although the following examples of the invention describe regeneration of palladium based acetylene reduction catalysts, one of skill in the art will recognize that the hydrogen stripping process of the present invention may be used to regenerate other types of catalysts that are used to hydrogenate acetylene. For example the present process could be used to regenerate acetylene hydrogenation catalysts which contain: Group VIII metals, such as nickel, cobalt, ruthenium, palladium, and platinum; Group VIB metals, such as chromium, molybdenum, and tungsten; or Group IB metals, such as copper, silver, or gold. However, the preferred catalyst for use in the present invention is a catalyst in which the primary active element is palladium, preferably one where palladium comprises approximately 0.01-0.5% by weight of the catalyst, more preferably 0.02-0.05%. A palladium content higher than about 0.5% could deteriorate at the temperatures used in the process of the present invention. Optionally the palladium may be combined with another metal, such as silver.

The catalyst metal is typically carried on a support such as silica or alumina.

The stripping procedure of the invention takes place at a temperature of from 315-400°C (600-750°F), preferably between about 315-372°C (600-700°F), and more preferably at about 350°C (662°F). In order to avoid deactivating the catalyst, especially a palladium based catalyst, or agglomerating the palladium, the temperature of the hydrogen stripping procedure should not exceed about 400°C. The temperature should be at

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least 315°C to achieve the substantially complete regeneration which is commercially desirable, and other process conditions will be readily determinable to enable this objective to be reached.

The pressure at which the stripping takes place may not be critical; however, the stripping preferably takes place between atmospheric pressure (0 psig) and 2.07 MPag (300 psig), and more preferably between atmospheric pressure and 345 kPag (50 psig). Lower cost hydrogen sources having a low content of hydrogen typically are more readily available at lower pressures. In the following examples, pressures of about 2.07 MPag and atmospheric pressure were used. Similarly, the time period required for stripping is not critical, save it should be sufficient to achieve substantially complete regeneration. One of skill in the art will recognize that the amount of time needed for the stripping procedure can be determined by monitoring the amount of hydrocarbon present in the catalyst until a minimum plateau level has been achieved. In the following examples, the stripping time ranged between 16-24 hrs.

The flow rate of the hydrogen through the catalyst should be such that the linear velocity through the catalyst should be at least about 15.2 cm/second (0.5 feet/second). This will ensure uniformity of reactant concentrations and temperatures throughout the reactor during regeneration. It has been found that lower velocities may be insufficient to achieve uniform regeneration of the catalyst. The parameter of linear velocity is used herein rather than, e.g., space velocity because linear velocity commonly is used to calculate dispersion and mixing phenomena in packed beds. For example, the axial and radial dispersion of reactant concentration are estimated by calculating Peclet numbers (James Carberry, "Chemical and Catalytic Reaction Engineering", p. 162). The linear velocity also is an important factor in controlling heat transfer in the reactor. Furthermore, linear velocities may differ even where the space velocity remains the same. For example, wide and shallow beds will have lower linear velocities than narrow and deep

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beds will have. However, narrow and deep beds will have a higher pressure drop than wide and shallow beds. Thus, it is desirable to specify either linear velocity or space velocity with the reactor L/D ratio to ensure proper design or scale up of the reactor.

It is a feature of the invention that substantially complete regeneration is achieved without the need for an additional or associated regeneration step, e.g., hydrocarbon wash or steam treat or, particularly, oxygenation. As shown in Example 1 which follows, the process of the invention enables catalyst to be re-used as fresh catalyst after regular hydrogen only regenerations of the catalytic metal sites, preferably in situ in the acetylene reduction reactor. Nevertheless it may be desirable from time to time to clean carbonaceous deposits from the support (as opposed to the catalyst metal) because hydrogen stripping does not remove all of the carbonaceous deposits from the support. Thus it is possible that an air burn may be desirable eventually in order to clean the support to prevent restriction of flow rate, pressure, etc. However, the number of air burns that may be employed to clean the supports in such a system will be much less than the frequent air burns that heretofore have been required to regenerate the catalyst. An infrequent air burn to clean the support will be much less intrusive and damaging than the frequent, repetitive air burns required in current catalyst regeneration processes.

The following examples illustrates the invention.

EXAMPLE 1

An aliquot of UCI G58B catalyst ($\text{Pd}/\text{Al}_2\text{O}_3$), deactivated after 200 hours of use as an acetylene hydrogenation catalyst in olefin stream treatment, was stripped with 10% H_2/Ar at linear velocity greater than 15.2 cm/sec and at a temperature which rose from room temperature to about 750°C (1382°F) at a heating rate of about 13 degrees C/min ($23.4^\circ\text{F}/\text{min}$). The carbona-

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ceous residues on the catalyst were analyzed both before and after hydrogen stripping by temperature programmed oxidation (TPO), which detected carbon oxide emission during the TPO burn while the reactor temperature was linearly increased. The TPO spectra of the spent catalyst before and after hydrogen stripping were plotted as Figure 1(a) and (b), respectively.

Before hydrogen stripping, two types of carbonaceous residues were present on the catalyst. A peak at about 400°C (750°F) represents carbonaceous residues that were present on and/or near palladium. A peak at about 510°C (950°F) represents carbonaceous residues that were present on the support. After hydrogen stripping, only one peak appeared at 550°C (1022°F). The presence of only this single peak after hydrogen stripping indicated that the carbonaceous residues that were on and/or near the palladium were removed by the hydrogen stripping. Since acetylene conversion occurs mainly on palladium sites in the catalyst, the removal of carbonaceous residues from the palladium can re-expose the palladium active sites and recover substantially all the activity of the palladium. The hydrocarbons that are stripped off the catalyst can be either recycled to the cracker or used as fuel gas.

EXAMPLE 2

A BASF HO11 catalyst (Pd/SiO_2) was subjected for 200 hours to the reaction conditions of 1.5% wt C_2H_2 (in an olefinic stream), 1.6 $\text{H}_2/\text{C}_2\text{H}_2$ molar ratio, 4000 gas hourly space velocity (GHSV), 2.07 MPag (300 psig), and about 66°C (151°F) average bed temperature. After 200 hours, the acetylene conversion of the catalyst decreased from 79% to 58%. The spent catalyst was then regenerated by hydrogen stripping for 16 hours with 5% H_2/N_2 at 2.07 MPag (300 psig) and greater than 15.2 cm/sec linear velocity in the reactor, and about 350°C (662°F). After the hydrogen stripping, the acetylene conversion of the catalyst was 78%. A comparison

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of the catalyst activity before and after hydrogen stripping is plotted in Figure 2. The results indicate that the hydrogen stripping at about 350°C (662°F) substantially fully regenerated the catalyst.

The temperature used during hydrogen stripping is preferably not too high or else the palladium will begin to agglomerate and will not achieve substantially complete regeneration using only a hydrogen treat step. For example, when the catalyst was further hydrogen stripped at about 420°C (788°F) for 16 hours, under otherwise the same conditions, the activity of the catalyst was reduced to 62% acetylene conversion -- a dramatic decrease in catalyst activity.

EXAMPLE 3

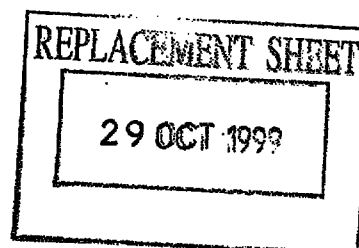
A spent UCI G58E catalyst (Pd/Ag/Al₂O₃) which had been used for acetylene hydrogenation in an ethylene stream was hydrogen stripped at about 350°C (662°F) and 1 atmosphere pressure with 9% H₂/N₂ at linear velocity in the reactor of greater than 15.2 cm/sec, for 24 hours. The performance of the hydrogen stripped catalyst was then compared to the performance of fresh catalyst at 70 hours into the activity test. The results are tabulated in Table I. The parameters of the activity test carried out in a normal hydrogenation reactor were 1.4% wt C₂H₂, 1.2 H₂/C₂H₂ molar ratio, 4900 GHSV, 2.07 MPag (300 psig), about 102°C (215°F) sand-bath temperature.

TABLE I

	Fresh	H ₂ Stripped
C ₂ H ₂ Conversion	80%	80%
Selectivity to C ₂ H ₄	57%	67%
Selectivity to C ₂ H ₆	32%	23%
Selectivity to C ₄ +	11%	10%
Deactivation Rate	-0.1%/hr	-0.2%/hr

As seen from Table I, the spent catalyst which had been hydrogen stripped according to the invention unexpectedly had a selectivity to ethylene that was 10 points better than the selectivity of the fresh catalyst. Also, the ethane make was substantially reduced after hydrogen stripping. This result suggests that a "de-edging" process may have occurred which reduced the number of palladium sites responsible for over hydrogenating acetylene/ethylene to ethane.

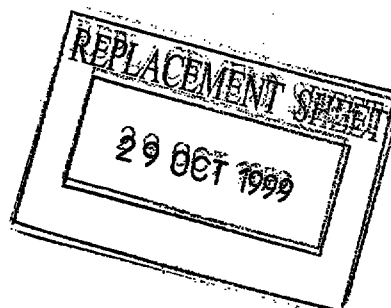
Although the deactivation rate was higher for the hydrogen stripped catalyst, the deactivation rate can be overcome by more frequent hydrogen stripping. Even if more frequent hydrogen stripping is required to regenerate catalyst, the present process may be less time consuming and less damaging to the catalyst than frequent air burns or other additional treatment steps.





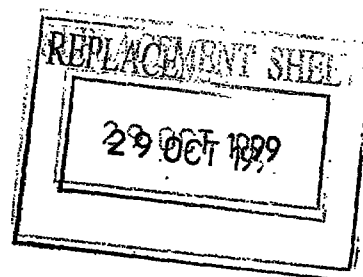
Claims

1. A method of substantially completely regenerating a catalyst that has been used to remove acetylenic impurities from an olefin stream and which has become at least partially deactivated by that use, which comprises substantially stripping the deactivated catalyst of carbonaceous deposits using hydrogen at a linear velocity of at least 15.2 cm/second (0.5 feet per second), at a temperature of from 315 - 400°C (599 - 750°F) and at other conditions such that substantially complete regeneration is effected, wherein said stripping is essentially the only regeneration treatment employed and occurs in the absence of an oxygenation step.
2. The method of claim 1 wherein the temperature is from 315 - 372°C (600 - 700°F), preferably about 350°C (662°F).
3. The method of claim 1 or 2 wherein the hydrogen stripping employs a gas comprising an inert gas, preferably nitrogen, and from 5 to 10% of hydrogen.
4. The method of any preceding claim wherein the catalyst comprises palladium, optionally together with another metal.
5. The method of claim 4 wherein the palladium comprises from 0.01 to 0.5 wt%, preferably from 0.02 to 0.05% of the catalyst.
6. The method of any preceding claim wherein the catalyst has been used to remove acetylenic impurities from ethylene.





7. The method of claim 6 wherein after regeneration the catalyst is used to remove acetylenic impurities from ethylene and the selectivity of the catalyst to ethylene is enhanced.
8. The method of any preceding claim wherein the catalyst comprises a silica or alumina support.



REGENERATION OF ACETYLENE CONVERTER CATALYSTS
BY HYDROGEN STRIPPING

ABSTRACT

An improved method for regenerating acetylene hydrogenation catalysts, particularly palladium based catalysts which have been used to remove acetylenic contaminants from ethylene, which method does not require an oxygenation or other pretreatment step, comprises stripping the spent catalyst with hydrogen at 315-400 °C and a linear hydrogen containing gas velocity of at least 15.2 cm/second, to achieve substantially complete regeneration.

