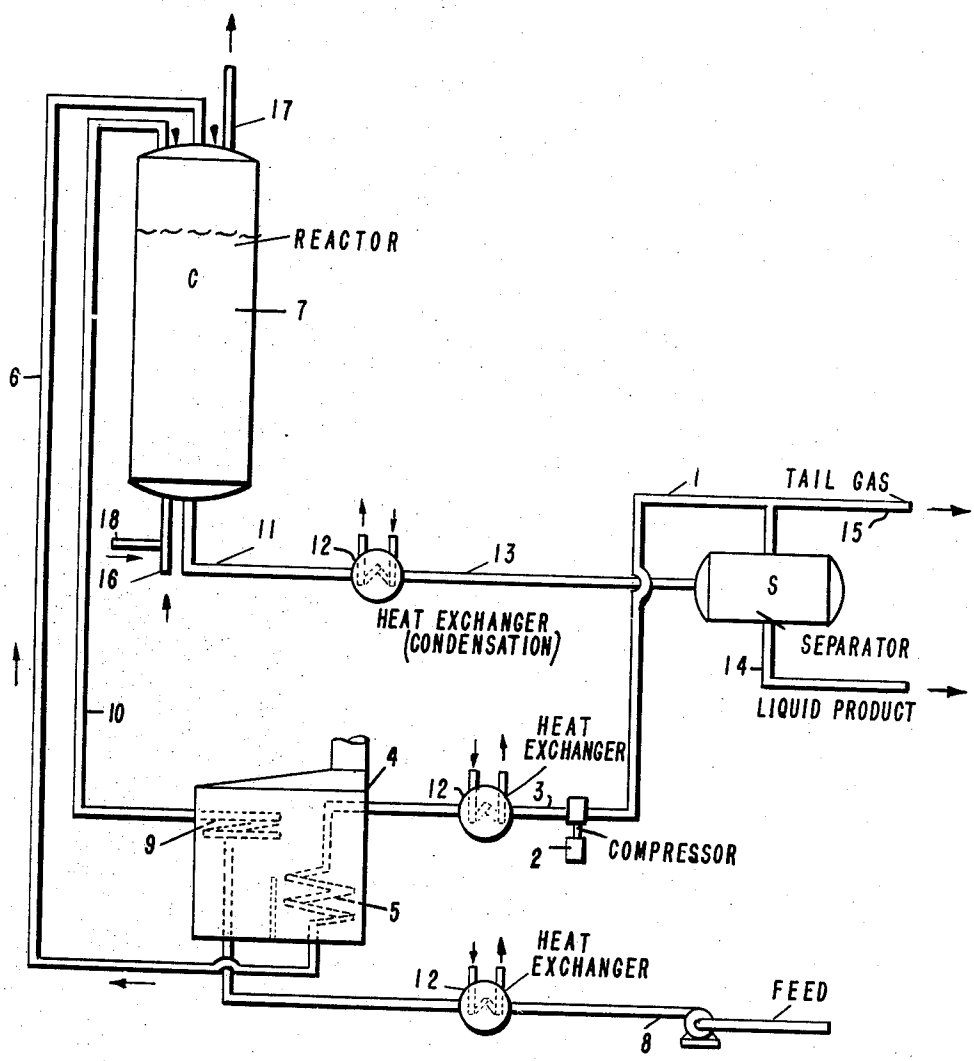
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HIGH PRESSURE CHLORINE REACTIVATION OF
ALUMINA SUPPORTED PLATINUM CATALYSTS
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HIGH PRESSURE CHLORINE REACTIVATION OF ALUMINA SUPPORTED PLATINUM CATALYSTS

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The present invention relates to improvements in the hydroforming of naphthas. More particularly, it relates to improved hydroforming processes wherein metal oxide-supported noble metal catalysts are reactivated through the utilization of gaseous halogen, particularly chlorine, under essentially static, superatmospheric conditions.

It is a matter of record and commercial practice to hydroform naphthas in the presence of a platinum catalyst. This platinum catalyst is usually supported on a suitable base, such as alumina, and may also contain a small amount of a promoter or stabilizer such as boria, phosphoric anhydride, silica, halides or organic acids. For instance, a commonly used composition of such catalyst is one containing from 0.001 to 2.0 weight percent platinum, the remainder being the alumina spacing agent or base. In place of alumina, other bases having mild cracking activity are used. In this hydroforming operation, a virgin naphthenic naphtha is contacted at elevated temperatures and pressures with the catalyst in the presence of added hydrogen. The function of the hydrogen is to repress the formation of carbonaceous deposits on the catalyst.

The operating conditions of the hydroforming operation are pressures in the range of 50 to 1000 p. s. i. g., usually 200 to 700 p. s. i. g., and temperatures in the range of 750°–1050° F., usually 900°–950° F. The hydrogen dilution can vary from about 1000 to 10,000 C. F./B.

The feed or charging stock to the hydroforming reactor can be a virgin naphtha, a cracked naphtha, a Fischer-Tropsch naphtha, or the like, and mixtures thereof. The feed stock is preheated alone or in admixture with recycle gas to reaction temperature. The endothermic heat of reaction is supplied by the cooling of charge stocks during the reaction. Normally two or more fixed bed reactors are used in series with intermediate reheating to maintain an average temperature high enough for the reaction to proceed.

The chemical reactions involved in the hydroforming process include dehydrogenation of naphthenes to the corresponding aromatics, isomerization of straight chain paraffins to form branched chain paraffins, isomerization of cyclic compounds such as ethylcyclopentane to form methylcyclohexane, and some aromatization, dealkylation and hydrocracking of paraffins. In a hydroforming operation which is conducted efficiently it is possible with the use of a proper catalyst and proper conditions of operation to hydroform a virgin naphtha having an octane number of about 50 to a hydroformate having an octane number up to as high as 95 to 98 and obtain yields of C_5+ hydrocarbons as high as 85%. The hydroforming can be carried out either by the fixed bed process or in accordance with the fluidized solid technique, e. g., see Serial No. 188,236, filed October 3, 1950, now Patent No. 2,689,823.

During the course of the hydroforming reaction carbonaceous deposits build up on the catalyst and consequently diminish its activity. These deposits are removed by subjecting the catalyst to combustion in an oxidizing atmosphere, i. e., air or other gas containing about 1 to 2% oxygen.

The platinum catalysts used in this process have been found to deactivate with usage for various reasons, among which are changes in the physical state of the platinum. Important factors in the latter, for example, are the increased size of the platinum crystals and the rate of platinum crystal growth. Contaminants such as other heavy metals also tend to deactivate the catalyst. The deactivation resulting from these factors should be distinguished from the simpler, more easily reversible, loss of activity of the catalyst due to carbonization from the hydroforming reaction itself, or diminution in hydrocracking activity due to loss of halide which can be restored by halide addition.

Changes in the platinum crystal lattice (size of unit cell) also account to a certain extent for catalyst deactivation. Although these changes are reversible under certain conditions of operation, the severe treatment required to alter the lattice eventually leads to an agglomeration of platinum crystallites which in the past has been considered an irreversible process. Normally, therefore, "spent" platinum catalysts are processed for the extraction, separation and recovery of the platinum which is then used to prepare fresh catalyst. This is, of course, an expensive operation, because of the platinum recovery charges and the cost for manufacturing new catalysts.

This invention provides an improved method of maintaining activity and selectivity of the catalyst in a fixed bed hydroforming process. The method comprises in combination treating freshly regenerated catalyst with halogen-containing gas under essentially static, superatmospheric conditions, stripping excess halogen from the catalyst, and reutilizing the thus-treated catalyst in the reaction zone wherein it is reduced and reactivated.

In accordance with this invention, commercially pure chlorine or dried chlorine, i. e., containing no more than 0.3 weight percent water, is injected into the freshly regenerated catalyst bed. The catalyst bed is essentially at atmospheric pressure after regeneration and is at a temperature of about 1000° F. The reactor system is blocked off and the pressure on the system due to the presence of gaseous chlorine is allowed to build up to about 175 p. s. i. g., at which pressure the reactor contains gaseous chlorine to the extent of about 2% by weight on catalyst. This pressure gradually decreases to about 130 pounds or less as the chlorine is reacted and/or adsorbed on the catalyst. The reactivation is essentially complete when the pressure has leveled off at the lower level. The residual chlorine is vented and the still hot reactor is stripped with air or flue gas to remove residual chlorine down to essentially the level of fresh catalyst, i. e., about 0.5 weight percent or less.

It is surprising to learn that gaseous halogens accomplish this effect, because gaseous hydrogen halide acids do not have the same effect on deactivated catalysts. Conversely, experimental data demonstrate that this reactivation is more than a so-called restoration of halogen content to the catalyst. The halogen content of the reactivated catalyst can be reduced to a level below that of the deactivated catalyst, but its activity remains markedly improved.

The noble metals for treatment in accordance with the present invention include platinum, palladium, gold, silver, iridium, rhodium, ruthenium, osmium, etc. These noble metals are generally associated and supported on a metal oxide and particularly an oxide of a metal in the left hand columns of groups III to VIII of the periodic table including particularly the oxides of silica, aluminum, titanium, zirconium, hafnium, thorium, vanadium, tantalum, chromium, molybdenum, tungsten, uranium,

manganese, zinc, cobalt, nickel, etc. It is understood that the catalyst can comprise two or more noble metals and/or two or more metal oxides. In still other cases, one or more activating components may be included in the catalyst. Particularly suitable is the platinum on alumina catalyst.

Various gaseous halogens can be utilized, i. e., chlorine, fluorine, and bromine. Chlorine is particularly preferred because of efficiency, cost, safety, and corrosion factors.

Alternatively the chlorine pressure can be maintained at 175 p. s. i. g., or even higher, by making up the before-discussed pressure loss with air, an oxygen-containing gas or oxygen, or by continuing to add chlorine during the reactivation. As a matter of fact, the presence of this air or oxygen appears to catalyze the desired reactivation. The air or oxygen and chlorine can be added up to a pressure corresponding to the design pressure rating of the unit.

The amount of chlorine utilized is in the range of 1 to 10 weight percent on catalyst and preferably 1 to 3 weight percent. For a typical catalyst consisting of 0.6% platinum on an alumina derived from the hydrolysis of aluminum alcoholate, the chlorine required in a static system for operation at 1000° F. and equivalent to 2 weight percent on catalyst would correspond to a pressure of about 175 p. s. i. g. The partial pressure of the chlorine gas would be 100% of the total pressure. All other things being equal, the higher the pressure, the more rapid the effect.

The stripping gases that can be used to reduce the halogen content include commonly available stripping gases such as hydrogen, nitrogen, flue gas, oxygen, air, steam, etc., or combinations thereof. The chloride content of the stripped catalyst is preferably 0.1 to 0.5 weight percent on catalyst.

The temperature of halogen treatment utilized is in the range of 600°–1200° F., and preferably 900°–1000° F. To eliminate heat input, the catalyst will generally be treated at temperatures prevailing in the unit. The preferred time interval of treatment is in the range of 5 to 60 minutes, but, as will be understood by those skilled in the art, the treating time can be varied to obtain the desired degree of reactivation.

This invention will be better understood by reference to the flow diagram shown in the drawing.

In the drawing, **7** represents a reactor, a single one being shown, containing a bed C of catalyst, the active component of which catalyst is a platinum group metal, such as platinum itself, carried on a suitable support such as active alumina. In the operation, hydrogen-containing recycle gas recovered from the crude product is withdrawn from a separator S via line **1**, then passed through compressor **2** into line **3**, from which it is charged through heat exchanger **12**, thence to a furnace **4**, heated in coil **5**, withdrawn and charged via line **6** into reactor **7**.

The hydrogen-containing gas enters the top of the reactor and passes downwardly through the bed C of catalyst.

The oil to be treated, which is ordinarily a virgin naphtha containing from 30 to 45% of naphthenes, is introduced in the present system through line **8**, is thereafter heated by heat exchange in **12** and in coil **9** in furnace **4** to a temperature of around 950° F., thereafter withdrawn from the furnace **4** through line **10** and charged into the bed of catalyst with the recycle gas.

Under conditions more fully set forth hereinafter, the desired conversion takes place, the principal chemical reaction being one in which naphthenes are dehydrogenated to the corresponding aromatic, as where methylcyclohexane is dehydrogenated to form toluene. The vapors and gases emerge from the reactor via line **11** to exchangers and coolers **12** wherein the normally liquid constituents are condensed and thereafter charged via line **13** into the separator S. The crude product is withdrawn from separator S via line **14** and delivered to product purification in equipment not shown while the net hydrogen-containing gas which is produced is sent to recovery not shown through line **15**. Recycle gas leaves through line **1** as indicated above.

As explained before, carbonaceous materials build up on the catalyst, making regeneration necessary. Suitable stripping gas such as nitrogen, scrubbed flue gas, or the like which serves to remove entrained or adsorbed hydrogen or hydrocarbon materials is injected through line **16** into reactor 7 and the stripping gas and stripped gases are taken overhead through line **17**. The catalyst is then regenerated by burning. A preferred means of carrying this out is by first burning with dilute air from line **18**, e. g., 1–2 mol percent oxygen at temperatures of about 650–800° F. The regeneration gases are taken off through outlet line **17** and cooled in a waste heat boiler (not shown) to remove heat of combustion. The cooled (to about 800° F.) flue gases are returned or recycled back to the reactor through line **16**. In an advantageous modification, after burning has been completed the temperature is then raised to 1100° F. at higher oxygen pressures, e. g., 100% air at 200 pounds pressure. The reactor is then vented to substantially atmospheric pressure. Pure chlorine-containing gas is introduced through line **18** into reactor **7**, where it contacts the regenerated catalyst at a temperature of around 1000° F. The reactor is blocked off from the rest of the system by closing the valves and the pressure on the system is allowed to build up by continuing to add chlorine until a pressure of about 175 p. s. i. g. is reached, at which pressure the reactor contains chlorine to the extent of about 2% by weight on catalyst. The pressure decreases to about 130 pounds or less as the chlorine is reacted and/or adsorbed on the catalyst. The reactivation is essentially complete at the point where the pressure levels off and the remaining chlorine is vented off through line **17**. The still hot reactor is vented and stripped with air or flue gas which enters through line **16** or **18**. The catalyst is in turn finally activated by the contacting with hydrogen and/or hydrocarbon feed as the reaction is again initiated.

While it is not intended that the process of this invention be restricted to any proposed mechanism of operation, it is apparent that the chlorine reactivation treatment brings about a redistribution of the platinum crystallites resulting in an increase in the specific platinum surface area and thus the activity of the catalyst.

In the hydroforming process itself the feed stock is preheated to reaction temperature, which may be 800°–1000° F., preferably about 875°–950° F. To avoid thermal degradation, time should be minimized in the transfer or feed inlet lines. The preheated feed stock may be supplied to the reaction vessel in admixture with hydrogen-rich recycle gas or it may be introduced separately as shown. The recycle gas, which contains from about 80 to 99 volume percent hydrogen, is also preheated to reaction temperatures of about 800°–1000° F., preferably about 875°–950° F., prior to the introduction thereof into inlet line **4**. It may be supplied to the reaction vessel in admixture with the preheated feed stock or may be introduced separately. The recycle gas should be circulated through the reactor at a rate of from about 1000 to 10,000 cubic feet per barrel of naphtha feed. The amount of recycle gas added is preferably the minimum amount that will suffice to carry the necessary heat of reaction into the reaction zone and keep the carbon formation at a satisfactory low level.

Space velocity or the weight in pounds of feed charged per hour per pound of catalyst in the reactor depends upon the temperature, activity level, or platinum content of the catalyst, the character of the feed stock, and the desired octane number of the product. Space velocity for a platinum on alumina gel can vary, for example,

from about 0.5 wt. oil/hr./wt. cat. to about 10 wt. oil/hr./wt. cat.

In order to explain the invention more fully, the following conditions of operation of the various components are set forth below and in the examples.

Hydroforming conditions

	Preferred	Range	Example
Catalyst Composition	0.6% Pt on Al_2O_3.	0.001-2% Pt on Al_2O_3.	0.6% Pt.
Inlet Reactor Temperature, ° F.	875-925	850-1,000	900.
Pressure, p. s. i. g.	200-500	50-1,000	200.
Cu. ft. of recycled gas fed/bbl. of oil.	4,000-6,000	1,000-10,000	5,000.

Regeneration conditions

	Preferred	Range	Example
Temperature, ° F	900-1,110	700-1,200	1,000
Pressure, p. s. i. g	5-400	0-700	200
Residence time, hours	1-5	0.25-20	4

Chlorine treatment conditions

	Preferred	Range	Example
Treat:			
Temperature, ° F	900-1,000	600-1,200	1,000
Pressure, p. s. i. g	100-220	10-1,300	175
Cl_2 Partial Pressure, p. s. i. g	130-230	1-1,000	175
Wt. Percent Cl_2 on Catalyst	1-3	1-10	2
Time of Treatment, minutes	10-60	5-240	20
Stripping:			
Temperature, ° F	800-1,000	600-1,200	1,000
Time, hours	1-4	0.5-10	3
Pressure, p. s. i. g	0-50	0-1,000	5
Wt. Percent Cl_2 on Stripped Catalyst	0.1-0.5	.01-1	0.5

Separate nozzles can be used for the injection of chlorine to the system rather than utilizing the larger nozzles required for feed injection. This effects operating economies because it minimizes the amount of equipment exposed to the corrosive action of chlorine.

Air blow-back can be used to remove chlorine from the larger equipment lines where its presence is unnecessary.

A guard chamber of alumina can be utilized immediately before the body of catalyst in order to protect the latter from products of metal corrosion.

Corrosion problems can be minimized, especially as regards metal corrosion products contaminating the catalyst, by various types of reactor design. One such means is to have the reactor wall so constructed that ceramic material constitutes the internal surface. This can be followed by a bonded alloy and then carbon steel with a normal insulation binding outside of the shell. This type of construction helps prevent corrosion products from contaminating the catalyst and also protects the shell itself.

Among the advantages of the process of this invention is the fact that only a very limited amount of cold material is added to the hot reaction system. The hot reactor and catalyst serve as their own heat supply and no loss in temperature takes place during the reaction period. Other processes, using once-through flowing air to dilute the chlorine, for example, would cool the catalyst bed as much as 200° during the reaction period. No excess equipment is needed over that conventionally utilized in hydroforming processes. The use of pure chlorine normally results in a dry system which eliminates any problems of drying of reactants or materials.

It is to be understood that this invention is not limited to the specific examples, which have been offered merely as illustrations, and that modifications may be made without departing from the spirit of this invention.

What is claimed is:

1. In a fixed bed process for hydroforming petroleum fractions at a pressure in the range of 50 to 1000 p. s. i. g. using an alumina supported hydroforming platinum catalyst which becomes deactivated during the process and contains carbonaceous deposits which are burned off by oxidation in a regeneration step at elevated temperatures and pressures, the improvement which comprises the steps of venting to atmospheric pressure the reactor containing said hot regenerated catalyst at a temperature in the range of 600° to 1200° F., building up the pressure in the reactor with gaseous chlorine to a static chlorine partial pressure in the range of 130 to 230 p. s. i. g. with the reactor vent line closed and reacting chlorine with said catalyst under said static conditions, venting the reactor to substantially atmospheric pressure and stripping the thus treated catalyst to remove excess chlorine therefrom to a level from 0.01 to 1 wt. percent based on the supported catalyst and reutilizing the thus treated catalyst in the hydroforming process.

2. The process of claim 1 in which the gaseous chlorine is utilized in an amount of about 2 weight percent under a pressure of about 175 pounds p. s. i. g.

3. The process of claim 1 in which an oxygen containing gas is added to the closed reactor during said chlorine treatment to compensate for chlorine absorbed by reaction with said catalyst.

References Cited in the file of this patent

UNITED STATES PATENTS

2,488,744	Snyder	Nov. 22, 1949
2,606,878	Haensel	Aug. 12, 1952
2,642,384	Cox	June 16, 1953
2,651,599	Watts et al.	Sept. 8, 1953
2,746,909	Hemminger	May 22, 1956

FOREIGN PATENTS

115,333	Germany	Oct. 31, 1900
20,915	Great Britain	July 9, 1903