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HIGH PRESSURE CHLORINE REACTIVATION OF ALUMINA SUPPORTED PLATINUM CATALYSTS


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3 Claims. (Cl. 196—50)

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 boron, phosphoric anhydride, silica, halides or organic acids.

For instance, a commonly used composition of such catalytic system consists of a metal, such as platinum, supported on a base such as alumina. The base is usually present in an amount of 1 to 20% by weight on the catalyst. This is usually supported in a reactor, which is subjected to a temperature and pressure such that the reactant mixture of naphtha and hydrogen will react to form the desired products such as paraffins and/or naphthenes.

In the present invention, the catalyst is subjected 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 palladium 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-reactivated 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 50 psig at a pressure above 1000° F. The pressure decreases to about 130 pounds or less as the chlorine is released for adsorption 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 II to VIII of the periodic table including particularly the oxides of silica, alumina, 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 halogenes can be utilized, i.e., chlorine, fluorine, and bromine. Chlorine is particularly preferred because of efficiency, cost, safety, and corrosion factors. It is understood that the chlorine pressure can be maintained at about 175 p.s.i. g. or 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 0.66% platinum on alumina derived from the hydrolysis of aluminum chloride, 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, 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°F to 1200°F, and preferably 900°F to 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 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 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 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 strip gas mixture 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 supply 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 adding 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 reaction 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 reaction treatment brings about a redistribution of the platinum crystallites resulting in an increase in the 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°F to 1000°F, preferably about 875°F to 950°F. The material 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°F to 1000°F, preferably about 875°F to 950°F, prior to the introduction thereof into 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 1000 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

<table>
<thead>
<tr>
<th>Catalyst Composition</th>
<th>Preferred</th>
<th>Range</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.6% Pt on</td>
<td>0.1%–1.5% Pt</td>
<td>0.2% Pt.</td>
</tr>
<tr>
<td>Column Temperature</td>
<td>0.5–1.5%</td>
<td>475–925</td>
<td>600</td>
</tr>
<tr>
<td>Pressure, p.s.i.g</td>
<td>200–500</td>
<td>0–1,000</td>
<td>500</td>
</tr>
<tr>
<td>Oil temperature, °F</td>
<td>4,000–6,000</td>
<td>1,000–6,000</td>
<td>5,000</td>
</tr>
</tbody>
</table>

### Regeneration conditions

<table>
<thead>
<tr>
<th>Temperature, °F</th>
<th>Preferred Range</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>900–1,100</td>
<td>700–1,200</td>
<td>1,000</td>
</tr>
<tr>
<td>Pressure, p.s.i.g</td>
<td>2–50</td>
<td>0–70</td>
</tr>
<tr>
<td>Residence time, hours</td>
<td>1–3</td>
<td>0.5–20</td>
</tr>
</tbody>
</table>

### Chlorine treatment conditions

<table>
<thead>
<tr>
<th>Treat</th>
<th>Preferred Range</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F</td>
<td>600–1,000</td>
<td>600–1,200</td>
</tr>
<tr>
<td>Pressure, p.s.i.g</td>
<td>100–200</td>
<td>150–300</td>
</tr>
<tr>
<td>Wt. Percent Cl₂ on Catalyst</td>
<td>0.1–0.5</td>
<td>0.1–1</td>
</tr>
<tr>
<td>Time Treatment, minutes</td>
<td>10–30</td>
<td>15–45</td>
</tr>
<tr>
<td>Stripper</td>
<td>Temperature, °F</td>
<td>600–1,000</td>
</tr>
<tr>
<td>Pressure, p.s.i.g</td>
<td>0–50</td>
<td>0–5</td>
</tr>
<tr>
<td>Wt. Percent Cl₂ on Stripped Catalyst</td>
<td>0.1–0.3</td>
<td>0.1–1</td>
</tr>
</tbody>
</table>

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. A fixed bed process for hydroforming petroleum fractions at a pressure in the range of 50 to 1,000 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 1,200° 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.

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