Optimized Pretreatment Procedures For Reforming Catalysts.

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ABSTRACT

Optimized Pretreatment Procedures For Reforming Catalyst

Platinum/rhenium and platinum/tin catalysts continue to play a major role in the reforming of petroleum naphthas to produce gasoline, hydrogen and petrochemical feedstock. In the last twenty years, with the introduction of skewed, unbalanced or high rhenium catalysts, a greater need has developed to optimize pretreatment procedures which would lead to full utilization of these catalysts.

Over the past ten years, a number of significant technological improvements have been made such as sulfur removal technologies to ensure that high rhenium catalysts can perform optimally in the reforming of naphthas. Despite the application of sulfur control technologies, in some cases, refiners still experience sub-par performances with their high rhenium catalysts.

There are several factors that can impact Pt/Re catalysts performance such as improper chloride and sulfur management programs, inadequate catalyst regenerations, high contaminants concentrations, and poor activations. This paper will address some aspects of catalysts activation for maximizing the catalytic performances of reforming catalysts. In these studies a modest effort has been made to generate fundamental and pilot unit evaluations data for pretreated high rhenium and platinum/tin catalysts. The pilot unit data showed that high rhenium catalysts should perform satisfactorily with proper applications of catalyst activation procedures.
**INTRODUCTION**

Platinum/rhenium (1) and platinum/tin (2) are the major types of bimetallic catalysts in use in the reforming of petroleum naphthas. Platinum/rhenium composites are used in semi-regenerative reformers whilst platinum/tin are the catalysts of choice for continuous catalytic regeneration (CCR) units. In the last ten years, high rhenium and mixed or staged platinum/rhenium catalyst systems have been used in reformers to optimize the performance of the combination catalytic system (3). Terms such as balanced, unbalanced, skewed and high rhenium have been coined to describe current platinum/rhenium catalyst types used in semi-regenerative reformers.

The term "balanced" is often used by some to describe a Pt/Re catalyst composite in which the rhenium to platinum molar ratio is approximately one. Thus, a 0.3 wt. % Pt/0.3 wt. % Re catalyst is referred to as a balanced catalyst, and the "high rhenium" designation is reserved for those Pt/Re catalysts for which the rhenium to platinum is greater than one and is preferably about 2. Often, in a semi-regenerative reformer, a balanced catalyst is used in the lead one or two reactors and the rest of the reactors are filled with high rhenium catalysts. This arrangement is sometimes referred to as a staged catalytic system (4).

High rhenium catalysts, in combination with appropriate liquid or vapor phase sulfur removal technologies, usually exhibit longer cycle lengths relative to the balanced catalysts (5,6,7). In some cases, however, refiners have not benefited from the use of high rhenium catalysts due to poor performances leading to short cycles, poor reformate, aromatics and hydrogen yields. In those special cases, the performances of the high rhenium catalysts have been characterized by high gas make and low weighted average bed temperature deltas for the reactor.

For reformers with on line catalyst samplers, it is often possible to monitor changes in the physical and chemical states of the catalyst relative to fresh. Contaminants such as iron, sodium, and silicon are typical, and depending on the concentrations, the contaminants can adversely affect catalyst performance. Sometimes, chloride and sulfur management practices are not satisfactory as can be gauged
by sulfur and chloride concentrations on the catalysts. Overall, periodic technical service of the reformer should aid in identifying catalyst performance issues relatable to easily identifiable causes.

However, for catalyst performance debits relatable to inadequate activation of the catalysts, there are only indirect methods of assessing the state of the catalyst. Carbon monoxide, hydrogen and other adsorbates have been used in chemisorption studies to assess the number of available metal sites on the catalyst. Temperature programmed reduction (TPR) studies have also been used.

Fresh and activated Pt/Re catalysts have been studied extensively over the years by workers such as Johnson and LeRoy (8), Bertolacini and Pellet (9), Wagstaff and Prins (10), McNicol (11), Charcossett (12), Isaac and Petersen (13) and Sachtler(14). These workers have shown that platinum and rhenium can exist as bimetallic clusters and the reductions of the platinum and rhenium to the zerovalent states are dependent on the moisture content during reduction. In addition, there seems to be unanimous agreement that platinum is easily reduced to the zerovalent state at about 500 to 600 F. and that rhenium reducibility is an issue with most of the rhenium reduction occurring in the 750 to 1022 F. range.

Scelza et. al's TPR studies (15) are typical of the outstanding work done as they were able to show the effects of small changes in chloride content during Pt and Pt/Re catalysts preparations on the reduction of the metals. In this work, we have used as a working hypothesis, the possibility that poor activations, and more specifically, inadequate reductions of the Pt/Re catalysts in "clean" reformers could be causing the poor performances observed with high rhenium catalysts.

Test runs have been conducted on fresh and activated or pretreated Pt/Re and Pt/Sn catalysts to show that properly activated high rhenium catalysts should perform as advertised. The work so far has been confined to first cycle evaluations, and it should be extended to high rhenium catalyst samples that have undergone multi-cycle naphtha reforming in a commercial unit. However, preliminary results with first cycle, activated high rhenium catalyst are highly encouraging and show that with proper activation, expected performance benefits of high rhenium catalysts can be realized in naphtha reforming. As mentioned earlier, the study should be extended to include multi-cycle Pt/Re catalyst
samples in accordance with the advice of Bickles and Do as contained in their recent paper (19).

EXPERIMENTAL

Catalyst

Commercial grade Pt/Re and Pt/Sn catalyst samples were used in these studies. Catalysts were prepared via standard manufacturing procedures involving impregnating special gamma aluminas with precursor salt and acidic solutions to deposit required metals and chloride on the supports. The samples were then dried and calcined. The composition of the Pt/Re catalyst was 0.22 % Pt/0.42 % Re/1.0 % Cl with a BET surface area of 210 m$^2$/gm and a bulk density of about 48 pounds per cubic feet. The composition of the Pt/Sn was 0.38 % Pt/0.30 % Sn/1.0 % Cl with a BET surface area of about 210 m$^2$/gm and a bulk density of 32 pound per cubic feet.

Catalyst Activation

Prior to utilizing the catalyst samples in test runs, some of the samples were activated using pretreatment procedures that were basically similar in principle and sequence to those practised in commercial units. Catalyst samples were charged into a specially dedicated, isothermal, high pressure, catalyst activation unit, and dried between room temperature and 800 F. in flowing nitrogen. During the drying, the heat up rate of the catalyst bed was maintained at 100 degrees Fahrenheit per hour.

At 800 F., a 5% oxygen/nitrogen gas mixture was introduced and reactor pressure raised to 300 psig. to initiate the air soak, rejuvenation or re-dispersion phase of the activation. Reactor temperature was raised to 975 F. at 50 degrees F. per hour, and then maintained at 975 degrees F. for 10 hours. During the holding period, chloride was added to about 0.1 wt. % level on the catalyst. This effectively increased catalyst chloride to about 1.1 wt. %.

The reactor temperature was then reduced to 900 F. or 950 F. as required, oxygen was purged out, and hydrogen introduced to initiate
reduction. The catalyst was reduced over a ten hour period. After reduction, samples of Pt/Re and Pt/Sn were submitted for CO chemisorption and TPR studies. The results of the CO and TPR studies are not included in this report. They showed essentially that total CO chemisorbed were similar for the fresh and activated Pt/Re catalysts.

For the Pt/Re catalyst, the reduction was followed by sulfiding with a 2.0 vol. % hydrogen sulfide/hydrogen gas mixture to deposit 0.15 wt. % sulfur on the catalyst. The Pt/Sn catalyst was not subjected to sulfiding. Catalyst samples were then analyzed and characterized prior to use in the test runs to ensure that chloride, sulfur and carbon contents were within specifications.

Test Runs

Heptane Test

Fresh and activated Pt/Re samples were tested in a 0.56 in. ID microreactor, fitted with a 0.125 in. OD thermowell. 5 grams of catalyst charge was used and test conditions were: 900 F., 100 psig., 4 WHSV and 5 hydrogen to hydrocarbon molar ratio. Heptane was the feed used for a quick assessment of the effect of reduction on high Pt/Re catalyst performance. Reactor effluent was separated into gas and liquid portions, and analyzed via Carle GC for refinery gas analysis and HP 5890 for naphtha liquids.

Constant Octane Test

Constant octane test runs were conducted in a 0.74 in. ID reactor, equipped with a 0.25 in. thermowell. 50 grams of catalyst charge was used and test conditions for the Pt/Re runs were: 255 psig., 98 RON, 4 WHSV and 3.0 hydrogen to hydrocarbon molar ratio. A low sulfur (0.13 wppm) paraffinic feed was used. Gravity, ASTM D-86 distillation and composition of the feed are given in Table 1.

For the Pt/Re runs hydrogen and naphtha were introduced into the reactor at 825 F. and test conditions were maintained for 18 hours before raising reactor temperature to produce 98 RON reformate liquids. Once this was achieved, reactor temperature was then
raised to compensate for catalyst deactivation and ensure that test runs were conducted at about 98 RON. During data reduction, a limited kinetic model correlation package was used to correct reactor temperatures, C5+ reformates and other desired product yields for deviations in operation from the 98 RON target.

For the Pt/Sn runs, test conditions were: 100 psig., 98 RON, 2 WHSV and 6.0 hydrogen to hydrocarbon molar ratio. Catalyst samples were aged at 800 F. for 48 hours before initiating testing at the reactor temperature required to produce 98 RON C5+ reformate.

RESULTS

Based on results of TPR studies by other workers (13, 15) cited earlier, it was reasoned that improved reduction of the high rhenium catalyst should lead to better performance of the high rhenium composite. Initial test runs were, therefore, conducted on fresh (labelled as "Unact"), and activated samples of high rhenium catalysts. One of the activated samples (Std) was subjected to standard activation as described earlier with metals reduction being effected at 900 F. The second sample was activated in a similar manner with reduction at 950 F. This sample is referred to as "Hi T" in the studies.

Total gas make data for the catalysts from the heptane test runs are shown in Figure 2. They show that the higher undesirable gases, methane through butanes, were produced by the unactivated sample. The high rhenium catalyst which had been subjected to the 950 F. reduction gave directionally lower gas. Based on this result, and similar data not shown on aromatics and hydrogen, we decided to conduct constant octane runs on a paraffinic naphtha to provide some supporting data. From the preliminary heptane reforming test data, it appeared that high temperature reductions could enhance the performance of high rhenium catalysts.

Data for three constant octane runs conducted on the same set of catalysts used in the heptane runs are given in Figures 3 through 7. In Figure 3, the unactivated catalyst's temperature requirements to make constant 98 RON reformate were excessive compared to those
required by Std and Hi T Pt/Re catalysts. The performance of the unactivated catalyst was similar to those observed in the use of high rhenium in some reformers. Temperature requirements of the Std and Hi T Pt/Re catalysts were essentially equivalent. In addition, activated catalysts reformate (C5+), total aromatics and benzene, toluene and xylene yields were consistently higher than those of the unactivated sample. Start of run (SOR) and end of run (EOR) inspections are given in Table 2 for the catalysts. They show that the 950 F. reduced catalyst made much less carbon than the unactivated and standard activated samples. With respect to the standard Pt/Re, the carbon advantage of the 950 F. Hi T is not as obvious since the run length of the Std Pt/Re was about 30% longer. However, it appears that higher temperature (950 F.) reduction could enhance the performance of high rhenium catalysts.

Carbon monoxide chemisorption studies were conducted on samples of activated Pt/Re taken after the rejuvenation step in the activation procedure, and on the fresh sample. The data did not show the expected differences as the total CO chemisorbed were essentially equivalent for the samples at 0.48 cc/gm after chemisorbing CO on 932 F. reduced samples. Similarly, the amounts of irreversible CO chemisorbed were also equivalent at about 0.15 cc/gm. A detailed chemisorption study should be conducted using CO and other adsorbates to better define differences between activated and unactivated high rhenium Pt/Re catalysts.

It was our desire to extend this study to include data from runs on activated multi-cycle high rhenium catalyst samples from a commercial reformer. However, this was not done and it is highly recommended that such a study be conducted with the necessary accompaniment of physical and chemical characterizations to assess the influence of impurities on Pt/Re catalyst performance which could negate the effects of the high temperature reduction enhancement observed in the study reported in this paper.

To ensure that the basic standard activation procedure used in our studies was good enough for other platinum containing catalysts, the procedure was applied to a plant produced Pt/Sn catalyst. As discussed earlier, the sulfiding step was not applied as it is not required for Pt/Sn catalysts. Results from the studies are shown in Figures 9 and 10. Pt/Sn A and C are similar plant produced samples that were not subjected to activation other than about a one hour reduction at 800 F. prior to introduction of oil during the test run.
Pt/Sn CA is a sample of Pt/Sn C which had been treated using the standard activation procedure. Based on the data in Figures 9 and 10, it is evident that the performance of activated Pt/Sn C was enhanced demonstrating that the basic standard activation procedure is excellent. SOR and EOR inspections of fresh and activated Pt/Sn C catalysts are given in Table 3.

DISCUSSION

Test data in Figures 3 through 7 on the unactivated high rhenium catalyst showed that some very poor performances can be expected with poorly activated high rhenium catalysts. The activity and selectivity performance data were similar to those reported by some refiners for operation in their reformers. BTX, total aromatics and total gas yields were as expected for the activated and unactivated samples of the high rhenium catalyst. The unactivated high rhenium catalyst activity and C5+ selectivity performance were essentially similar to those expected of a monometallic platinum catalyst.

Based on previous TPR studies results cited (14, 15), the platinum moiety of the bimetallic was most likely reduced at 800 F. in the short period of contact with hydrogen. At the 800 F reduction, it is likely that only a small fraction of the rhenium component was reduced to the zerovalent state. Since most of the rhenium component was not reduced, rhenium could not effectively aid in the suppression of coke precursors, hence, the higher coke (6.10 wt. %) observed for the unactivated Pt/Re relative to the 4.20 wt. % coke on the Hi T Pt/Re catalyst. Inspections data for SOR and EOR Pt/Re catalysts from the runs are given in Table 2.

Total gas make showed that the unsulfided, unactivated high rhenium Pt/Re catalyst exhibited a greater degree of hydrogenolysis than observed with the activated Pt/Re catalysts. The data are in agreement with those of Jothimurugesan which showed that unsulfided Pt/Re catalysts exhibited higher hydrogenolysis than its sulfided analog. Jothimurugesan (16), and Bickle et. al. (17) also showed that sulfided rhenium could cause some suppression of hydrogenolysis over Pt/Re catalysts.
Based on the data in Figures 6 and 7, total aromatics and BTX for the unactivated catalyst are much lower than those of the activated. The results suggest that two different reactions are negatively impacting the aromatization activity of the unactivated catalyst. Excessive hydrogenolysis of the paraffins, and coke deposition on specific dehydrogenation sites on platinum could be affecting the overall set of paraffin dehydrocyclization reactions. In the simplified reaction pathway for the aromatization of heptane by Oblad et. al (19), it was shown that hydrogenolysis of the heptane and excessive coke deposition could affect the paraffin aromatization activity of the platinum/alumina catalyst.

Overall, test runs data showed that poorly activated Pt/Re would exhibit activity and selectivity performances that were essentially similar to those of a monometallic catalyst. To ensure that the high rhenium catalysts perform satisfactorily, as advertised, in commercial reformers, it is recommended that they are used in low sulfur (< 0.5 wppm feed sulfur) naphtha reforming, and subjected to proper and optimal catalyst activations including, if necessary, high temperature reductions. Directionally, in terms of rhenium reduction, the high temperature reduction can only enhance the performance of the Pt/Re catalysts.
REFERENCES


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<tr>
<td>Gravity, API</td>
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<tr>
<td>Sulfur, wppm</td>
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<td>-------------------</td>
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<tr>
<td>Cl, wt. %</td>
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<td>S, wt. %</td>
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**Table 2**

Pt/Re Catalyst Inspections
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<th>Catalyst State</th>
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<th>Activated</th>
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<td>0.04</td>
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<tr>
<td>Sulfur, wt. %</td>
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<td>0.01</td>
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<tr>
<td>Chloride, wt. %</td>
<td>0.93</td>
<td>0.81</td>
<td>1.00</td>
<td>0.83</td>
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FIGURE 1
TPR of Pt/Al₂O₃, Re/Al₂O₃ and Pt-Re/Al₂O₃

SCELZA et al.: Pt-Re/Al₂O₃ CATALYSTS
Figure 2
Pt/Re Total Gas Make\Heptane Feed

Total Gas, Wt. %

- Pt/Re Unact
+ Pt/Re Std
* Pt/Re Hi T

Time, Hours

900 F., 100 psig, 4.0 WHSV, 5/1 H2/HC
Figure 3
Pt/Re Catalyst Activities
Figure 4
C5+ Yields for Pt/Re Catalyst

C5+ Yield, vol. %

Time, Hours

Pt/Re Unact.  Pt/Re Std.  Pt/Re Hi T.
Figure 5
Activated Pt/Re Exhibited Equivalent Selectivity to Gas Products

Total Gas, Wt. %

Time, Hours

- Pt/Re Unact.
- Pt/Re Std
- Pt/Re Hi T
Figure 6
Pt/Re Total Aromatics Yield

Total Aromatics, Wt. %

Time, Hours

- - Pt/Re Unact  • Pt/Re Std  * Pt/Re Hi T.
Figure 7
Pt/Re BTX Yields

BTX Yields, Wt. %

- Pt/Re Unact
- Pt/Re Std
- Pt/Re Hi T.

Time, Hours

60 ~-------------------------------------------~
40 ~-------------------------------------------~
20 ~-------------------------------------------~
0 ~-------------------------------------------~

0 20 40 60 80 100 120 140 160
Figure 9
Activation Enhances Activity of Pt/Sn Catalyst

Temp. F.

Time, Hours

Pt/Sn C
Pt/Sn B
Pt/Sn CA
Figure 10
Pt/Sn Catalyst C5+ Selectivity

C5+ Yield, Vol %

Time, Hours

- Pt/Sn C
- Pt/Sn B
- Pt/Sn CA