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STEVE METRO, UOP LLC, A HONEYWELL COMPANY, USA, AND GUIHE LI,
PetroChina LiaoYang PetroChemical Company (PLPC), China, DISCUSS
HOW CCR PLATFORMING™ CATALYSTS TARGET A RANGE OF OBJECTIVES.
Catalytic naphtha reforming maintains its position as a major process in the petroleum refinery with several new units added annually to an installed base of over 250 units worldwide. Catalytic naphtha reforming units provide hydrogen for clean fuels, high octane reformate product for gasoline, and aromatics for petrochemicals production. The recent economic climate and the impact of government regulations has impacted the role of the reformer in various regions differently.

In developed regions such as North America, Europe, and Japan, refinery utilizations and reformate demand are generally down due to a number of regulatory and market trends. The response by some refiners has been to reduce the octane and/or throughput to their reformers. However, reforming is still critical to making gasoline and providing hydrogen for hydrotreating various refinery streams and for hydrocracking needed for growing diesel demand. Most refiners have indicated that yields are still the top priority regardless of whether the reforming unit is operating at normal or reduced severities. The target is to achieve the most productivity at a given severity. Catalyst activity is also important for process unit flexibility in order to increase severity when needed to take advantage of market opportunities.

In contrast, the Asia Pacific region is dominated by the emergence of China, India and other rapidly growing economies. Fuels and aromatics demand growth in these emerging regions is driving major investments and creating a highly supportive environment for UOP continuous catalyst regeneration (CCR) Platforming™ process units. The Middle East, with their advantaged economies and low feedstock costs, are also adding reforming capacity for motor fuel and aromatics production. For existing reforming units, increasing the naphtha feed to the reformer can produce additional quantities of gasoline or aromatics. In addition, more aromatics and hydrogen can be produced by operating at higher severity (higher temperature and octane operations). These reforming units can achieve these types of objectives with more active CCR Platforming catalysts that operate at a lower temperature.

**Catalyst solutions**

With the first UOP fixed bed Platforming unit starting up in 1949, and well over 200 modern UOP CCR Platforming units started up since 1971, UOP has been the leader in reforming technology development. In step with numerous process, equipment, and control innovations, UOP has also developed many catalysts needed to push production limits further and maximise profitability. UOP catalysts have been designed to provide both high activity and high yields of reformate, hydrogen, and aromatics for motor fuel and aromatic applications. Specifically formulated high yield catalysts offer an extra boost to higher yields.
while higher density catalysts offer the highest activity and the ability to overcome catalyst pinning constraints. The latter properties are ideal for increasing aromatic and/or C₅₊ production by processing more naphtha feed in the unit.

The UOP R-230 series CCR Platforming catalysts were commercialised in the year 2000 with specific objectives of providing good activity, increased yields and significantly lower coke make than the industry standard UOP R-134 and R-132 CCR Platforming catalysts at that time. A lower coke catalyst offers the ability to debottleneck CCR Platforming units operating at a coke burning limit, thus allowing higher octane operation, increased feed rate, options to process heavier or cracked naphtha feedstocks, or a reduction in the H₂/HC ratio.

The development of the R-230 series catalysts involved improving the catalyst alumina base and the metal-to-acid ratio. The alumina base was modified through new manufacturing techniques and the acid function was modified to match the new base. As a result, compared to the R-130 series catalysts, the coke production was reduced by 20 - 25%, while the C₅₊ yield was increased by 0.5 - 0.6 wt%. The R-234 catalyst and higher Pt version R-232 catalyst have now been applied in over 100 CCR Platforming units worldwide and continue to provide higher yields and lower coke for a wide range of customers and applications.

**Case study: PLPC refinery, China**

With compounded annual growth rates near 10%, China has been rapidly building oil refineries for aromatics and motor fuel production. China has adopted UOP CCR Platforming process technology for high quality reformate production, with the first unit starting up in 1985. Over 30 UOP CCR reforming units are now operating in China, with several new units added each year to meet growing market needs.

Recently, the PLPC Liaoyang refinery in China was interested in increasing the production of total aromatics at their current feed rates. The refinery has a UOP CCR Platforming unit operating at 50 psig (3.5 kg/cm²) with a feed rate of approximately 12 000 bpd (79.5 m³/hr) and a pressurised regenerator. The naphtha feed to the unit is typically a combination of cracked and straight run naphthas with a paraffin content of nominally 50 wt%. The catalyst in the unit prior to the catalyst changeout was a non-UOP catalyst. This catalyst was not able to achieve the desired octane target and displayed higher than desired coke production. After PLPC evaluated the available catalyst options, the FR-234 catalyst was selected to replace the non-UOP catalyst. FR-234 is a UOP CCR Platforming catalyst manufactured in Fushun, China by UOP's manufacturing partner Fushun Petrochemical Company.

The FR-234 catalyst was loaded into the unit on 7th September 2007 and feed was cut into the unit just two days later. A series of performance tests were conducted from 31st October to 2nd November, averaged, and then compared to the guaranteed values. Figure 1 shows the C₅₊ and A₅ recoveries for each performance test and the averages. Table 1 shows that the averaged test results exceeded the expected performance.

There was an interest to make a start of run comparison between the previous non-UOP catalyst employed and the FR-234 catalyst, but a direct comparison was not possible due to differences in process conditions, severity, and feed composition. However, a comparison was made using the UOP Platforming kinetic model. The performance of the FR-234 catalyst was predicted at the process conditions, octane and feed composition corresponding to the performance tests of the non-UOP catalyst when it was first loaded in the unit. Table 2 shows that the FR-234 catalyst out performed the previous non-UOP catalyst by a large percentage for H₂ and total aromatics yields. With the increased yields, an economic benefit of 42.5 million China Yuan Renminbi (US$ 6.42 million) per year was obtained.

**High density catalysts**

Another UOP Platforming innovation was the development of a higher density CCR reforming catalyst. The higher density UOP R-264 CCR reforming catalyst was commercialised in 2004 with the objective of allowing CCR units to increase throughput for increased C₅₊, H₂, and aromatic product volumes. In addition, the higher Pt version R-262 catalyst was commercialised in 2007 for select higher severity operations. Compared to the UOP's R-130 series catalysts, the R-260 series catalysts have higher density, a tailored pore structure to minimise very small pores, reoptimised metal/acid balance, and increased strength. These properties result in higher activity, less coke production, good coke burning rates in the regenerator, and reduced catalyst fines.

Furthermore, the R-264 catalyst can debottleneck units that are running up against a catalyst pinning constraint. Catalyst pinning is the condition where the force from the horizontal flow of feed across the downflowing catalyst results in the catalyst being pinned against the centre pipe screen. Pinning must be avoided because it causes flow maldistributions inside the reactor, leading to lower conversion and much higher coke make. Since the R-264 catalyst is denser, the downward force of flowing catalyst is larger thus allowing a higher feed throughput across the catalyst. As a result, the capacity in many CCR Platforming units can be increased by approximately 10% at constant H₂/HC ratio and by up to 20% at constant recycle gas flow. Increasing the naphtha feed rate will lead to increased product volumes and profitability.

The R-264 and R-262 catalysts have been loaded in over 50 units to date, in both UOP Platforming units and non-UOP designed continuous regeneration reforming units, with the majority in the former. R-264 catalyst is the catalyst of choice for new CCR Platforming units, particularly those designed for aromatics production. These flexible catalysts can be run in high activity and high yield modes by adjusting the amount of chloride on the catalyst during catalyst regeneration. In the high yield mode, some activity is traded for obtaining higher C₅₊, H₂, and aromatic yields. The chloride level is maintained at levels in which full Pt redispersion is attained with excellent stability. The high yield mode can be useful for maximising the desired products in situations where the feed rate has been reduced to the unit.

**Catalyst life**

An important factor in catalyst selection is how long the catalyst can operate in the unit before a changeout is required. A study was conducted to identify the number of commercial UOP CCR Platforming units that had 10+ years of catalyst life. Figure 2 shows that approximately 50 units have achieved catalyst life of 10 or more years. There have been two units that achieved over 20 year catalyst life. The long catalyst life is attributed to the stability of UOP’s alumina base, chloride retention properties.

| Table 1. Test results from performance test versus guaranteed values |
|-------------------|-------------------|-------------------|
| Target/guarantee | R-234 average performance |
| Material balance, % | 98 - 102 | 99.53 |
| C₅₊ liquid recovery, wt% | 87.32 | 67.76 |
| H₂ production, wt% | 3.99 | 4.16 |
| A₅ liquid recovery, wt% | 73.38 | 76.69 |
| RONC | 105 | >105** |

**Table 2. Comparison of FR-234 catalyst versus previous non-UOP catalyst**

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<th>Non-UOP catalyst</th>
<th>R-234 performance estimated at previous conditions</th>
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<tbody>
<tr>
<td>H₂ yield, wt%</td>
<td>4.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Total aromatics yield, wt%</td>
<td>74.5</td>
<td>76.2</td>
</tr>
<tr>
<td>RON</td>
<td>103.6</td>
<td>103.6</td>
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maintaining performance over time, catalyst flexibility to meet objectives and robust regenerability.

**Promoted high yield CCR catalysts**

In 2001, a high yield UOP R-274 catalyst was commercialised providing 0.5 - 1.0 wt% higher C₂⁺ yields versus the R-234 catalyst for low pressure operations. The improvement in yields was accomplished by the addition of a promoter metal with the main function of modifying the acid function and secondary function of modifying the metal function. In terms of acidity, the promoter improves the selectivity of paraffin cyclisation reactions relative to paraffin cracking reactions. By reducing the acid cracking of paraffins, liquid petroleum gas (LPG) production is reduced and the amount of reactants available for conversion to aromatics is increased. In terms of the metal function, the promoter reduces the metal hydrogenolysis activity (metal cracking) resulting in reduced formation of methane and ethane.

UOP has researched the addition of promoters extensively over the years and has concluded that the selection of a promoter for a commercial CCR reforming unit is dependent on:

- The impact on the performance including yields, activity, stability and coke make.
- The ability of the promoter to function correctly and consistently through many oxidation and reduction cycles.
- Not detrimentally impacting other catalyst properties such as chloride retention.

In continuous operations, the catalyst moves from the reaction zone to the regenerator where the coke is burned at elevated temperatures, followed by reoxychlorination to redisperse the Pt and restore the target chloride level. The catalyst then passes to a drying zone, then to the reduction zone, and finally back to the reactor in optimal state.

Utilising thermodynamic calculations, experimental regeneration studies and physical property testing, it was found that not all promoters are suited for the repeated oxidation/reduction cycles. For example, one promoter was found advantageous for performance (e.g. increased yield) but found to be unstable on the catalyst: the promoter was volatile under typical reaction and regeneration conditions. As a second example, another promoter was found to benefit yields and surface area stability but it significantly debited the chloride retention properties of the alumina base.

With over 15 loads in operation, the promoter metal in the UOP R-274 catalyst has been proven in commercial units to provide higher performance and to remain intact on the catalyst over a large number of cycles. As an example, Table 3 shows that the promoter level for the R-274 catalysts currently in operation in two CCR Platforming units after many years is essentially the same concentration as start of run. in

<table>
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<th>Refiner</th>
<th>Years in unit</th>
<th>% promoter on catalyst</th>
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<tr>
<td>1</td>
<td>2.8</td>
<td>98%</td>
</tr>
<tr>
<td>2</td>
<td>6.5</td>
<td>97%</td>
</tr>
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Table 3. Relative promoter levels in R-274 catalyst in UOP commercial units

Recently, pilot plant testing was conducted for a refiner using their naphtha feeds tested, the new R-254 catalyst has been measured to be 7 ºF (4 ºC) more active with the same yield selectivities as the R-274 catalyst. The testing compared the performance of the R-274 and new R-254 catalysts versus the R-234 catalyst. For the naphtha tested, Figure 3 and Table 4 show that the yields and coke were similar for the R-254 and R-274 catalysts but the R-254 catalyst was 4 ºC more active than R-274. The results also demonstrate the effect of the promoter in reducing the C₃₊ yields (reduced acid cracking) and lowering the C₃₊C₄ yields (reduced metal cracking).

A second new high yield catalyst has been formulated using UOP’s high density alumina base. The new R-284 catalyst has the same density, metals and chloride levels as the R-264 catalyst but with the addition of the same promoter as used in the R-254 and R-274 catalysts. The activity of the R-284 catalyst is 3 ºF (2 ºC) more active with higher yields as compared to the R-254 catalyst. For current reformers, the higher density of R-284 can aid in processing high throughputs if constrained by catalyst pinning. For new CCR Platforming units, the performance and properties of the R-284 catalyst make it an ideal candidate to produce maximum aromatic and xylene yields for petrochemical production.

**New high yield CCR catalysts**

The next step for improving the high yield R-274 catalyst was to retain the selectivity advantages but increase the activity. Maintaining use of the same proven promoter but modifying the addition procedure of the promoter to the alumina base have accomplished this. For the naphtha feeds tested, the new R-254 catalyst has been measured to be 7 ºF (4 ºC) more active with the same yield selectivities as the R-274 catalyst.

Recently, pilot plant testing was conducted for a refiner using their feed at the conditions representative of their CCR Platforming unit operation: 102 RON, 130 psig (9.14 kg/cm²), 2.8 hr⁻¹ and 2.0 H₂/HC. The testing compared the performance of the R-274 and new R-254 catalysts versus the R-234 catalyst. For the naphtha tested, Figure 3 and Table 4 show that the yields and coke were similar for the R-254 and R-274 catalysts but the R-254 catalyst was 4 ºC more active than R-274. The results also demonstrate the effect of the promoter in reducing the C₃₊C₄ yields (reduced acid cracking) and lowering the C₃₊C₄ yields (reduced metal cracking).

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Motor fuels case study

Economic calculations were made for a motor fuel case comparing the incremental profitability of the R-254 catalyst versus the R-234 catalyst. Pilot plant yield results and the UOP Platforming kinetic model was utilised to generate the product profiles at the average motor fuel conditions: 22 000 bpd (146 m³/hr), 106 psig (7.45 kg/cm²), 2.3 H₂/HC, and naphtha with 55.9 wt% paraffins, 31.4 wt% naphthenes, and 12.7 wt% aromatics. The products were valued using a standard US Gulf Coast economic set. Figure 4 shows that the R-254 catalyst provides a net benefit of +US$ 1.1 million/y at 102 RON, +US$ 0.8 million/y at 99 RON and +US$ 0.7 million/y at 96 RON. This demonstrates that the R-254 catalyst still provides a benefit for reforming units that are operating at reduced severity due to lower gasoline demand, including increased ethanol blending in the gasoline pool in some markets.

Conclusion

The recent economic climate, impact of government regulations, and new market trends have impacted the role of the reformer in different regions to varying degrees. Some refiners are reducing the severity of the reformer while others are pushing their units for more production of C₅₊, H₂ and aromatics. A variety of catalysts including UOP’s R-234, R-264 and the new high yield R-254 and R-284 catalysts are available for providing the best yield, activity and coke performance based upon unit objectives. Local manufacture and supply of UOP catalysts such as FR-234 bring value to emerging regions such as China as demonstrated by the PLPC refinery case study.