

# Consider advanced multi-promoted catalysts to optimize reformers

## Improved catalyst systems strike a new balance to increase yields with greater selectivity for end-products

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Catalytic reforming accounts for a large share (28%) of the world's gasoline production. It is the most important source of aromatics for the petrochemical industry. Reforming is also a major source of refinery-based hydrogen, for which demand is growing rapidly due to escalating hydrotreatment needs. Although the state of the art has advanced remarkably improvements in catalyst selectivity, activity and stability have significant impact on refinery economics. The incentive to improve reforming catalyst formulations is as high as ever. Catalyst development continues to be a major activity among catalyst suppliers.

**Ways to improve catalyst performance.** As the difference between feed cost and product value has enormous leverage in continuous catalyst regeneration (CCR) reformer economics, improvements in catalyst selectivity to produce better yields greatly enhance the unit's profitability. Two parameters can be controlled for better selectivity: *catalyst-chloride content* and *promoter-metal interaction*.

**Chloride content.** Controlling the chloride content is a function carried out in the operating unit. Lowering the chlorine content reduces the effect of the catalyst's acid-site function. In doing so, both liquefied petroleum gas (LPG) production and corrosion in the unit are reduced. For a chloride content reduction of 0.1 wt%, an empirical increase of 0.3 wt% in C<sub>5</sub><sup>+</sup> product is expected. This said, a minimum chloride content of 0.8 wt% is needed to stabilize the catalyst and, especially in the case of CCR reforming catalysts, to catalyze the extension of alkylcyclopentane rings to cyclohexane or alkylcyclohexane rings.

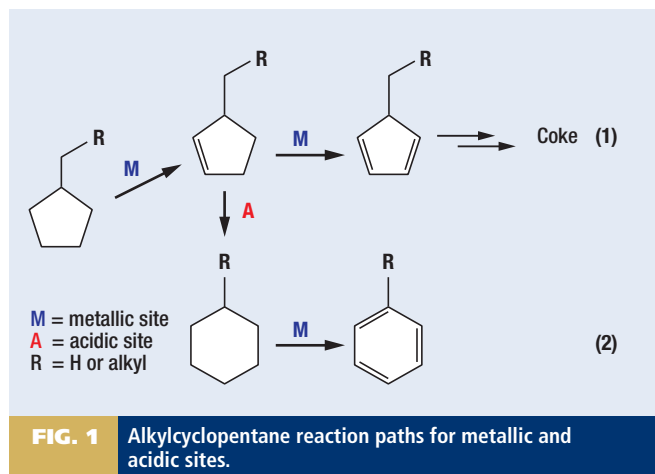
The reaction paths are representative of the desired and undesirable results (see Fig. 1). A deficit in acid-site function produces a full metallic mechanism (path 1) resulting in an alkylcyclopentadiene, which forms coke, a vicious cycle follows: catalyst activity diminishes and higher operating temperatures are required to maintain conversion. The higher temperatures impede catalyst selectivity, resulting in poorer yields, and the catalyst must be regenerated more often. If regenerator capacity is attained, the regenerator becomes a bottleneck.

The second and favored reaction pathway shows that, with optimum chloride content on the catalyst, cyclohexane or alkylcyclohexane is formed, preferably to the alkylcyclopentadiene. This allows ring dehydrogenation to the desired aromatic compound. Coke production is minimized as the aromatic is more stable than the alkylcyclopentadiene.

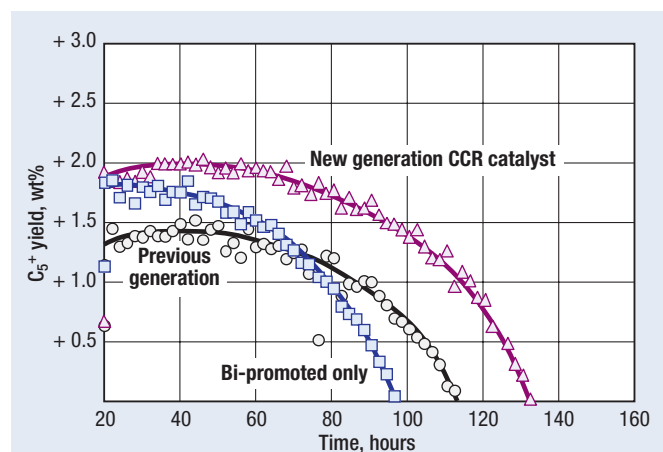
Research and development efforts to improve catalyst selectivity and activity by changing the promoter-metal interaction without compromising stability were successfully achieved. Thus, a new CCR catalyst generation has been developed comprising of a high-density family and a low-density family. These new promoters were chosen to reduce the coke precursor interactions and polyaromatics adsorption on the metallic cluster sites,<sup>1</sup> while reducing the hydrogenolysis activity of platinum.

**High-density family.** Results from bench-scale and micro-pilot plant testing indicated that adding a single promoter such as germanium was not enough to provide the targeted high selectivity and stability. Indeed, the selectivity enhancement attributed to the new promoter in the bi-promoted catalyst was offset by diminished stability. Tuning the dehydrocyclization and dehydrogenation activities was inseparable from degradation in coking activity. It was found that the new CCR catalysts benefited significantly from using a combination of different promoters, which controlled the increase in the activity for the desired reactions while minimizing coke precursor formation.

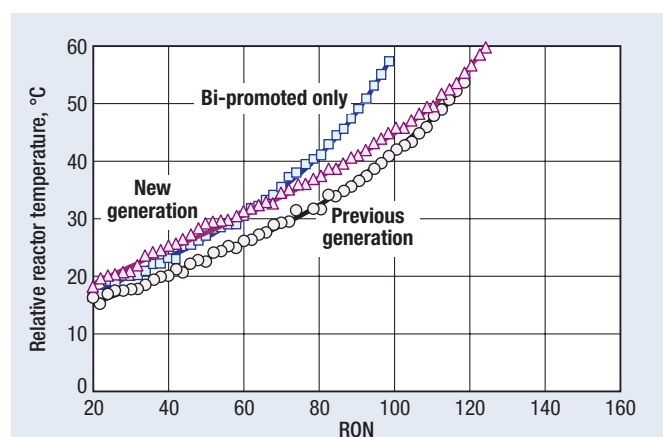
Figs. 2 and 3 illustrate these findings. The bi-promoted catalyst (in blue) did not maintain the same selectivity increase over the previous generation catalyst (in black) as that obtained within the first few hours of the test (Fig. 2). The new catalyst (in burgundy) showed it was stable relative to that of the previous generation.



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**FIG. 2** Relative  $C_5^+$  yield, wt% and stability are improved compared with the previous generation and the bi-promoted catalyst.



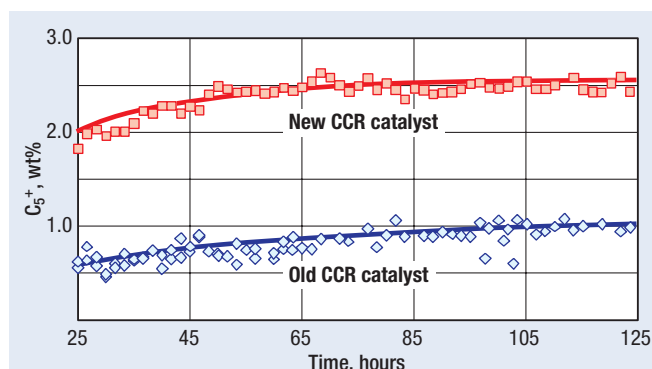
**FIG. 3** Long-term stability of the new generation catalyst is improved compared with that of the bi-promoted catalyst.

**TABLE 1. Comparison of CCR catalyst to previous generation and bi-promoted catalysts**

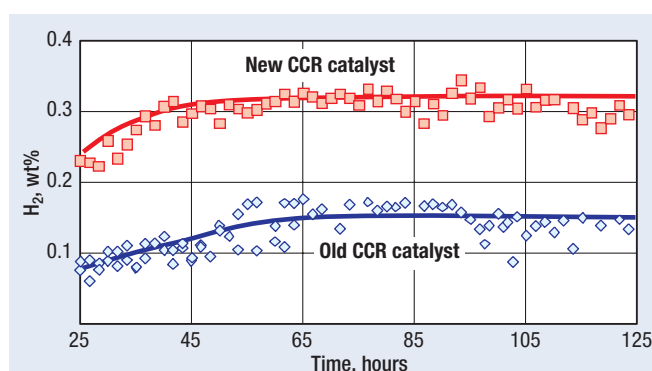
Yields, wt%	Previous generation	Bi-promoted only	New generation
Hydrogen	Base	Base + 0.1	Base + 0.1
$C_5^+$	Base	Base + 0.5	Base + 0.8
Aromatics	Base	Base + 0.6	Base + 0.7
Temp	Base (120 h)	Base + 20°C (100 h)	Base (120 h)
Coke	Base	+ 10%	-20%
Pressure = 3.5 barg, RON = 104, WHSV = 2.5/h, $H_2/HC = 4$ mol/mol			

The tests were performed in a multi-reactor unit allowing simultaneous testing of four catalysts in small amounts under realistic operating conditions. The effluent analysis was monitored by online gas chromatography, from which product yields and the research octane number (RON) were calculated. Tests were conducted at 3.5 barg, constant WHSV and a RON of 104. The temperature was automatically adjusted to maintain the targeted RON.

The  $C_5^+$  components yield is reported in Fig. 2 as a function of time while activity is represented by the temperature increase needed to maintain RON at 104 (Fig. 3). Combining the effect of different promoters in the new catalyst does not alter the  $C_5^+$  yield obtained with the bi-promoted catalyst but provides



**FIG. 4** Relative  $C_5^+$  yields for low-density catalysts with respect to time.



**FIG. 5** Relative hydrogen yields for low-density catalysts with respect to time.

extended stability as illustrated in Fig. 3. Table 1 summarizes the performance of these catalysts.

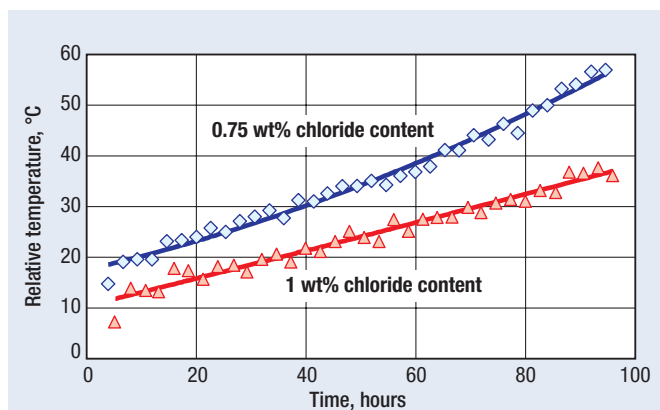
The higher stability while maintaining activity was achieved with a significant reduction in platinum (Pt) inventory. Moreover, as seen in Table 1, the new catalyst produces less coke. This gives the refiner added flexibility to consider processing thermally cracked naphthas, such as coker naphtha or when units are operated at higher severity: higher feedrates, lower recycle ratios or higher octane numbers.

Thermally cracked naphthas are known to produce higher amounts of coke than straight-run (SR) naphtha. For a unit designed to process SR naphtha as a feed, the reduced coke production will allow a refiner to treat thermally cracked naphtha without having to revamp the regenerator's coke burning capacity, as shown in Table 1.

Given the expected gains in either aromatics or  $C_5^+$  yields, and the different hydrogen partial pressures corresponding to operating pressure, four high-density catalysts were developed for the new CCR family.<sup>2</sup>

**Low-density family.** Based on the results obtained with the high-density family, a new multi-promoted catalyst on a low-density carrier was developed. Figs. 4 and 5 show that the multi-promoted low-density CCR catalyst outperforms the industrially proven CCR catalyst. Tested using same system as that used for the high-density family, conditions for the new multi-promoted CCR catalyst and previous-generation CCR catalysts were: 8 barg,  $H_2/HC = 3$  mol/mol, WHSV = 2.6 h<sup>-1</sup>, RON = 100.

The choice of multi-promoter doping for the low-density catalysts was again guided by the quest for higher  $C_5^+$  and  $H_2$  yields.



**FIG. 6** The low-chloride content of the catalyst negatively impacts the catalyst stability.

As pilot testing was performed at comparable chloride contents, the higher yield is not linked to chloride effects. The weight percent yield gains of 1.5 for C<sub>5</sub><sup>+</sup> and 0.16 for H<sub>2</sub> yields are linked directly to the doping.

The high-density and low-density catalyst performance is explained mainly by a modification of the Pt particle electronic density, which was confirmed by infrared (IR) spectroscopy. This affects the adsorption energies of the different compounds on the particles—in particular those of aromatic compounds, leading to a change in selectivity.

The promoters have also shown effects on support acidity, as they bring their own acidity or basicity. Controlling the support acidity helped to inhibit cracking reactions that are responsible for the lack of selectivity on liquid effluents.

**Activity adjustment.** It is well known that varying the catalyst's chloride content will change, for a given set of operating conditions, its yields and activity. As a rule of thumb, a variation of 0.1 wt % chloride content on the catalyst will change the activity by 2°C and change the C<sub>5</sub><sup>+</sup> yield by 0.3 wt%–0.4 wt %. When seeking high yields, such an approach has intrinsic limitations. Too-low chloride levels strongly diminish catalyst stability as the ring extension of the alkylcyclopentane to an alkylcyclohexane is not efficient.

Two catalysts with different chloride loadings were tested in the same unit as previously described. The test conditions are 3.5 barg, RON = 104, WHSV = 2.5/h, H<sub>2</sub>/HC = 4. The temperature increase needed to maintain a constant RON of 104 as a function of time is shown in Fig. 6. The low-chloride content curve shows that the catalyst's activity reduces (higher reactor temperature required) while its stability diminishes with time as compared to the higher-chloride content catalyst (red curve).

The low-chloride-content catalyst presents a gain in C<sub>5</sub><sup>+</sup> yields at shorter onstream times as shown in Fig. 7. This is explained by the low acidity on the surface that favors reforming reactions over acidic cracking. However, the low-chloride catalyst lacks stability; consequently, yield improvements do not last.

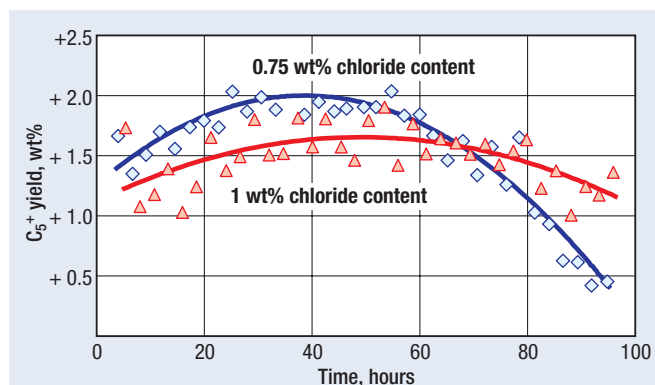
With the new catalyst for which carrier acidity has been optimized, the trade-off between activity and selectivity was changed. A new set of empirical rules was established after testing the new CCR catalyst family with different chloride loadings.

For a variation of 0.1 wt% chloride content on the catalyst, the activity will change by 4°C to 5°C, while the C<sub>5</sub><sup>+</sup> yield will only

**TABLE 2. Product values for new and old generation CCR catalysts, \$/ton**

H <sub>2</sub>	2,100
C <sub>5</sub> <sup>+</sup>	520
Fuel gas	300
LPG	450

change by 0.15 wt%. Therefore, these new catalysts offer greater flexibility to the refinery seeking activity improvement but with almost no reduction in selectivity. Moreover, as the hydrothermal stability of the carrier was drastically improved, the high initial chloride retention will be maintained throughout regeneration.



**FIG. 7** The low-chloride catalyst shows a gain in selectivity initially but after the selectivity diminishes significantly over time.

**Economics.** Based on these improvements, comparative economic studies were done to determine the profit one can expect using the new CCR catalyst instead of the previous catalyst generation. One such study was based on a 40,000-bpsd CCR reformer having a total catalyst inventory of 120 tons. The assumptions were that the investment, feedrate and recycle ratio were identical for both catalyst systems. Therefore, the operating cost differences between the new and older CCR catalysts are equal, and the main cost difference between the catalyst systems was due to the lower amount of Pt.

For the C<sub>5</sub><sup>+</sup> product, the higher H<sub>2</sub> and C<sub>5</sub><sup>+</sup> yields were taken into account together with the lower fuel gas and LPG production. Table 2 lists the product values.

The differential profitability ( $\Delta$ profit) is discounted over a seven-year period using Eq. 1:

$$\Delta\text{profit}^{\text{Discounted}} = \sum_{\text{year}=1}^N \frac{\Delta(\text{Profit per year})}{(1+i/100)^{\text{year}}} - C_1 \quad (1)$$

Where:

- C<sub>1</sub> Difference in platinum costs between initial catalyst load and replacement catalyst
- i Discount rate; 10%
- N Number of years taken into account.

With these assumptions, the discounted profit was found to be almost \$21 million higher using the new CCR catalysts, or almost \$2 more per ton of feed. The payback time for the new CCR catalyst is estimated to be less than one year even without taking into account the savings received from its lower Pt content.

**Catalyst options.** Based on a better understanding of the links between catalyst properties and performance, and after carrying out extensive pilot testing, new multi-promoted CCR catalyst families were developed.<sup>2</sup> The main benefits of these new formulations are: higher yields at constant chloride content with

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higher profitability; greater stability that enables more flexibility for operations and lower operating costs; lower Pt inventory; and reduced utility consumption due to lower recycle ratios and higher chloride retention.

The low-coke production tendency of these new catalysts is a key factor when considering the changing nature of reformer feeds. For example, the amount of coke produced from thermally cracked naphtha is higher than that from SR naphtha. Considering the large number of new coker projects underway, using multi-promoted catalysts will allow existing CCR reformers to accept these new feeds without modifying the regenerator design. **HP**

### LITERATURE CITED

<sup>1</sup> Goda, A. M., M. Neurock, M. A. Barteau and J. G. Chen, *Surface Science*, Vol. 602, pp. 2513–2523, 2008.

<sup>2</sup> [www.axens.net](http://www.axens.net)—AR & CR Series Catalysts.



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