

## Catalysts

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# Choosing an FCCU CO promoter is no longer driven by NO<sub>x</sub> emissions

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Fluidized catalytic cracking units (FCCUs) form coke during the reaction that combusts in the regenerator and supplies heat for the process. The reactions can be full combustion to carbon dioxide (CO<sub>2</sub>) and water or partial combustion to carbon monoxide (CO) and water emissions. CO can further combust to CO<sub>2</sub>. An FCCU may utilize CO promoter additives to catalyze these reactions to:

- Meet environmental regulations on CO emissions
- Reduce afterburn, which occurs when CO and oxygen react in the dilute phase (or less commonly the flue gas line) of the regenerator. In the dilute phase, there is less catalyst to absorb the heat of combustion, potentially causing significant temperature increases above metallurgical limits.

Beyond the desired oxidation reactions, promoters also catalyze the unwanted reaction of nitrogen in the coke to form nitrogen oxides (NO<sub>x</sub>) (vs. N<sub>2</sub>). Depending on NO<sub>x</sub> restrictions, there are two types of platinum group metals (PGM):

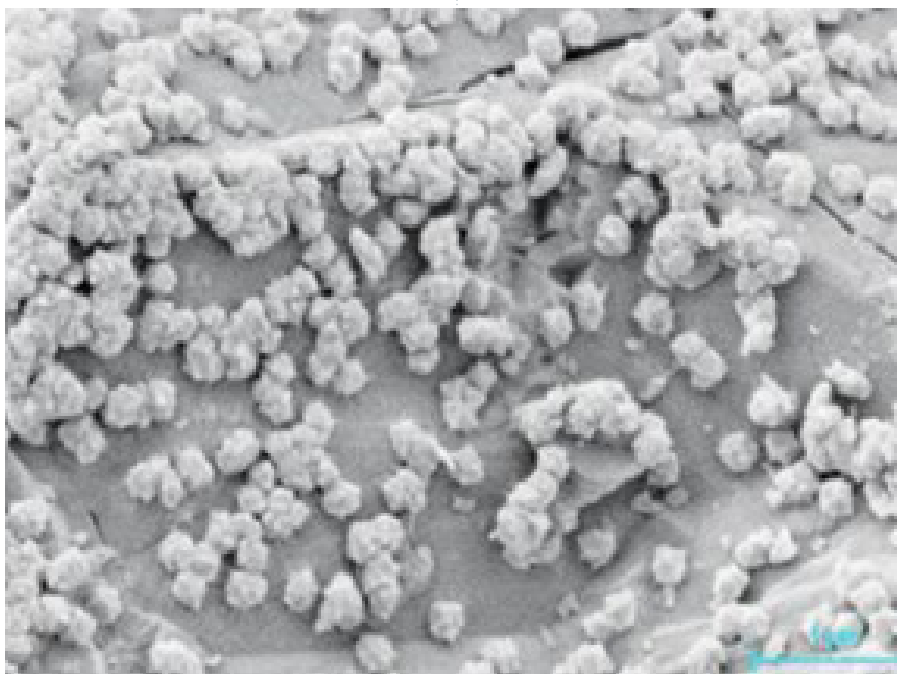
1. Platinum promoters that allow higher degrees of CO promotion but generate substantial NO<sub>x</sub>
2. Non-platinum promoters, which typically use palladium that generate comparably less NO<sub>x</sub> but are less effective in CO oxidation.

In early 2018, platinum and palladium both cost approximately \$1,000/troy ounce (oz t). At present, palladium is more than double the price of platinum.

As palladium-based catalysts tend to require more metal to achieve equivalent CO promotion, a palladium-based CO promoter is around \$25/lb more expensive than a platinum-based CO promoter due to metals cost alone. For example, an average unit uses 2 lb–5 lb of CO promoter additive per sT catalyst. At 5 sT/d, that could be more than \$200,000/yr higher costs to use a palladium promoter vs. a platinum promoter. Note: The metals are generally not considered recoverable. Given this, FCCUs will preferably use platinum-based CO promoters. Palladium is used by units that either have an environmental consent decree and/or cannot meet NO<sub>x</sub> emissions with platinum-based promoters.

## Novel promoters

Conventional promoters also have a short half-life (around a few days) due to metal sintering under high-temperature conditions in the FCCU. To mitigate these issues, a new generation of CO promoters has been developed. These novel promoters use a tuned PGM-support interaction, hindering sintering by anchoring PGM on the support. The resulting morphology modification (FIG. 1) improves promoter durability. Anchoring enables the ability to control PGM-oxygen interaction through oxygen on-demand shuttling. The products are designed to have optimized attrition, density and particle size distribution for use in the FCCU.



**FIG. 1.** The image, using a scanning electron microscope, shows the customized surface morphology of the CO promoter.

The co-authors' company has designed a novel, proprietary, durable platinum-based CO promoter that generates significantly less NO<sub>x</sub> vs. traditional platinum promoters. In laboratory testing, the proprietary CO promoter was compared to the latest generation of palladium and platinum promoters (TABLE 1). The proprietary promoter matched palladium promoter activity at 15% lower addition. The NO<sub>x</sub> generation increases about 10% when using palladium—in comparison, the platinum promoter generated 160% more NO<sub>x</sub> vs. the proprietary design. For most units, the proprietary CO promoter allows the choice between palladium vs. platinum to no longer be driven by NO<sub>x</sub> emissions constraints, but rather based on PGM pricing.

The first commercial adoption of the proprietary CO promoter was at CHS's Laurel refinery outside Billings, Montana. The refinery processes a severely hydrotreated vacuum gasoil feed and operates in full burn. The site previously used a preblended palladium-based promoter for NO<sub>x</sub> control. The proprietary promoter replaced the palladium promoter at a preblended 12.5% lower addition rate to achieve similar CO oxidation activity, while staying within the desired NO<sub>x</sub> limits. The afterburn decreased by half—from 6.67°C (44°F) to -5.56°C (22°F)—at a lower regenerator bed temperature (a shift to a lighter feed reduced bed temperature) (TABLE 2). Most importantly, the overall promoter cost (\$/d) decreased—a desired benefit in the COVID-19 economic environment.

## Takeaway

Modern platinum-based CO promoters have a price advantage over palladium-based promoters due to PGM pricing. However, NO<sub>x</sub> limits can inhibit the adoption of platinum promoters. The next-generation, proprietary platinum-based CO promoter generates less than 10% more NO<sub>x</sub> vs. palladium promoters. The technology's custom-tuned PGM-support significantly reduces sintering for enhanced CO promotion

durability. With this next-generation promoter, the choice between palladium or platinum promoters is no longer driven by NO<sub>x</sub> emissions constraints but rather by pricing and performance.

In the first commercial trial at the CHS Laurel refinery, the proprietary platinum-based CO promoter replaced a palladium-based promoter. The new platinum-based CO promoter yielded similar CO emissions, easily stayed within NO<sub>x</sub> constraints and reduced afterburn by 22°F, all at 12.5% lower addition rate. The proprietary platinum-based CO promoter enables refiners previously limited to high-priced palladium promoters to reduce operating expenses and improve performance. **HP**

## NOTES

<sup>a</sup> BASF's ENABLE™ CO promoter

<sup>b</sup> BASF'S CONQUERNOX®

## The Authors



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**TABLE 1.** Lab testing results for commercial palladium- and platinum-based promoters vs. the proprietary promoter<sup>a</sup>

	Palladium-based	Platinum-based	Proprietary promoter <sup>b</sup>
CO conversion, %	50	50	50
NO <sub>x</sub> conversion, %	75	200	82

**Note:** Samples were aged and normalized on CO conversion (%) basis. Aging: 12h, T<sub>max</sub> = 760°C, flow-through reactor: 10 min air, 10 min N<sub>2</sub>, 10 min H<sub>2</sub>, 10 min N<sub>2</sub>, constant 10% H<sub>2</sub>O-steam. Test: 99% spent catalyst + 1% promoter, 1 l/min, 2 vol% O<sub>2</sub>/N<sub>2</sub>, 700°C.

**TABLE 2.** CHS Laurel regenerator performance for the palladium-based CO promoter<sup>a</sup> and the novel platinum-based promoter<sup>b</sup>

Promoter	CO, mol%	NO <sub>x</sub> , ppm vol	Catalyst bed temperature, °F	Dilute phase temperature, °F	Afterburn, °F
Palladium-based CO promoter <sup>a</sup>	0.005 ± 0.002	35.1 ± 7.3	1,370 ± 6.2	1,354 ± 8.1	43.9 ± 6.7
Platinum-based CO promoter <sup>b</sup>	0.006 ± 0.002	40.3 ± 8.2	1,300 ± 4.9	1,322 ± 5.2	21.9 ± 6.7

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