

◆ COVER FEATURE ◆



# A RARE ALTERNATIVE

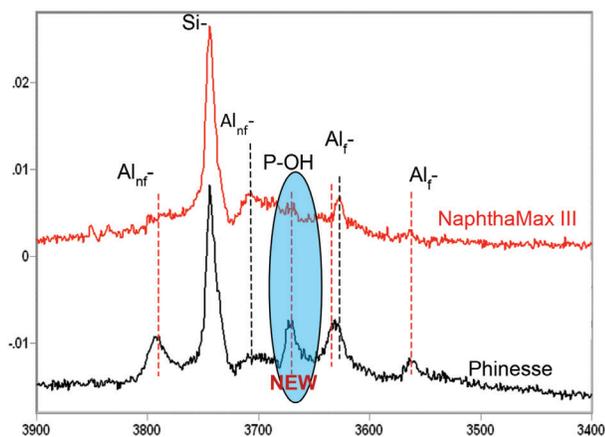


**Alexis Shackelford, Thomas Masak, Qi Fu, Gary M. Smith and Bilge Yilmaz, BASF Corporation, and Robert D. Culp and Piotr Gawecki, Shell Global Solutions,**  
discuss an alternative to rare earth elements in FCC catalysts.

**R**are earth (RE) elements have been utilised since the 1960s to stabilise Y zeolites used in fluidised catalytic cracking (FCC) catalysts. Of the RE elements, lanthanum is by far the most commonly used element in RE containing catalysts.<sup>1</sup> Cerium is also used in addition to lanthanum to an extent, with no current commercial FCC catalyst using solely cerium. China, which in 2010 provided 99% of the world's rare earth oxide (REO) supply, dramatically reduced export quotas that same year resulting in lanthanum prices increasing from US\$8/kg to a high of US\$140/kg in 2011. (As of 2015, China provides 93 - 96% of the world's REO and there are currently no export quotas).<sup>2</sup> In response to

this situation, BASF developed Phinisse™ FCC catalyst, which uses phosphorus modification for the stabilisation of Y zeolite. Phosphorus acts as an extra framework species to stabilise the Y zeolite framework, allowing lower REO content with no performance debits. This technology has been commercially demonstrated at the Shell Sarnia FCC unit.

Phinisse is the first BASF catalyst that uses phosphorus stabilisation on Y zeolite. Based upon BASF's proven Distributed Matrix Structure (DMS) technology,<sup>3</sup> Phinisse is designed for vacuum gas oil (VGO) feed applications and to give the same yield structure and activity as BASF's NaphthaMax III®<sup>4</sup> with 50% less RE.



**Figure 1.** Pyridine FT-IR analyses of Phinisse and 1% REO NaphthaMax III catalysts. Phinisse shows the creation of new acid sites, P-OH.

**Table 1.** Physical and chemical characterisation data for NaphthaMax® III and commercially produced Phinisse catalyst

	Phinisse	NaphthaMax III
REO, wt%	0.93	2.01
Total surface area (TSA), m <sup>2</sup> /g	284	278
Matrix surface area (MSA), m <sup>2</sup> /g	65	76
Unit cell size (UCS), Å	24.49	24.50
RE on zeolite ratio	3.07	7.15

**Table 2.** Conversion at cat/oil 4.5 and selectivities at constant conversion 75 wt%

	Phinisse	NaphthaMax III
Conv. @ C/O = 4.5, wt%	70.65	70.43
Total C <sub>2</sub> -, wt%	3.21	3.16
Liquefied petroleum gas (LPG), wt%	19.56	19.63
Gasoline, wt%	46.60	46.99
Light cycle oil (LCO), wt%	15.99	15.88
Bottoms, wt%	9.01	9.12
Coke, wt%	5.63	5.22
C <sub>3</sub> =/total C <sub>3</sub> s, wt/wt	0.81	0.82
C <sub>4</sub> =/total C <sub>4</sub> s, wt/wt	0.55	0.57

**Table 3.** Table comparing the fresh catalyst properties of Shell Sarnia's incumbent catalyst NaphthaMax to Phinisse showing Phinisse has similar properties at half the REO

	NaphthaMax	Phinisse	NaphthaMax III
TSA m <sup>2</sup> /g	BASE	BASE	BASE
REO wt%	2.00	1.00	2.00
Average particle size μm	75	76	76
Unit cell size (UCS) Å	24.57	24.53	24.53
Pore volume (PV) cc/g	0.33	0.33	0.33

The product was successfully scaled up and demonstrated in 2012 - 2013 at the Shell Sarnia refinery. This article discusses the results of that effort.

## Concept and development

Extensive work has been done to increase the hydrothermal stability of zeolites through the inclusion of rare earth ions. Rare earth ions (RE<sup>3+</sup>) are exchanged for Na<sup>+</sup> in Y zeolite to balance the negative charge in the catalyst framework (AlO<sub>2</sub><sup>-</sup> - SiO<sub>2</sub>). RE<sup>3+</sup> cations help retain acid sites under severe hydrothermal conditions of FCC operation to improve both the activity and the hydrothermal stability of the catalyst. Rare earth ions also promote hydrogen transfer so refiners can use RE<sup>3+</sup> loading to manipulate catalyst activity and selectivity. The resultant effect is higher gasoline yield at the expense of lower octane, lower LPG olefins yield, and higher delta coke when RE exchanged catalyst is used.<sup>5</sup>

Consideration of alternative elements that would function as rare earth elements in stabilising the zeolite Y framework has been a research topic of great interest for some time. When looking for an RE alternative, BASF research went back to the basics, starting with the periodic table of elements. Elements were first excluded if they were more expensive than RE, radioactive, toxic, gases, gave undesirable reactions at FCC conditions, or would melt at FCC conditions. Out of the short list of remaining elements BASF tested many options, with phosphorus giving the best results. Phosphorus modification serves a dual function of stabilisation and catalytic activity enhancement. Phosphorus is known to stabilise catalytic activity in zeolites and is commercially applied to FCC additives (e.g. ZSM-5) and methanol to olefins catalysts (e.g. ZSM-5). The phosphorus treated samples retain their acidity and activity much better than the untreated zeolite during the steaming treatment. The mechanism through which phosphorus increases the stability of the zeolite structure has been widely studied in academic literature. It was demonstrated that during steaming, more aluminum atoms remain attached to the framework due to Al-O-P chemical bond formation.<sup>6,7</sup>

BASF developed a novel way to apply phosphorus to BASF's proven DMS based materials.<sup>8,9</sup> Phosphorus not only increases catalyst activity but also increases hydrogen transfer giving the comparable yield performance as RE. Through a detailed pyridine FT-IR characterisation study comparing Phinisse with NaphthaMax III, the results showed that phosphorus stabilises the zeolite framework Al acid sites in both supercages and small cages, decreases the number of non-framework Al acid sites and introduces new P-OH acid sites (Figure 1).

The newly developed Phinisse catalyst was scaled up to manufacturing in 2011 and 2012. A catalyst sample obtained from commercial manufacturing was tested versus NaphthaMax III, BASF's state of the art maximum conversion VGO FCC catalyst. The samples were hydrothermally deactivated at 1450°F for 24 hours before testing. The catalytic evaluation was performed in an advance cracking evaluation (ACE®) unit at 1020°F with a gasoil feed with 0.79 wt% concarbon and 22 API.

During catalytic evaluation, Phinisse exhibited slightly higher activity despite having 50% less REO while no selectivity penalty was observed, as shown in Table 2.

## Commercial performance

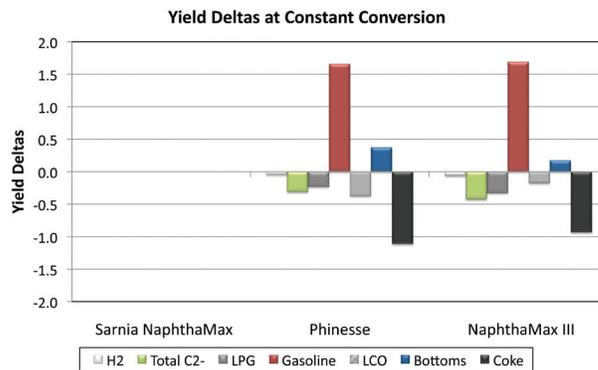
The first commercial trial of Phinisse was at Shell's Sarnia refinery in Ontario, Canada. This is a VGO unit, with a significant portion of the feed from Canadian conventional and synthetic crudes. The unit objectives were to maximise profits with liquefied petroleum gas (LPG) olefins, gasoline and light cycle oil (LCO) being highly valued.

At the time, the unit used BASF's NaphthaMax catalyst. BASF proposed Phinisse FCC catalyst with similar physicochemical properties as NaphthaMax but with half the REO. Catalyst properties for both NaphthaMax and Phinisse are shown in Table 3. In support of the trial, BASF tested three catalysts: NaphthaMax, the proposed Phinisse, and an equivalent NaphthaMax III catalyst at 2 wt% REO. As Phinisse is based on NaphthaMax III manufacturing, it was expected to have improved coke selectivity over the incumbent NaphthaMax catalyst. The NaphthaMax III catalyst was included in the testing to differentiate between differences due to the RE replacement technology and due to the NaphthaMax III technology. The three catalysts were deactivated using cyclic steaming to match the unit's equilibrium catalyst (Ecat) properties and then ACE tested. Figure 2 shows the results of this test. The delta yields at 75% conversion are shown off the base Sarnia NaphthaMax catalyst. Phinisse shows similar performance to NaphthaMax III, with half the REO, with both catalysts giving approximately 1 wt% lower coke yield resulting in 1.5 wt% higher gasoline yield compared to NaphthaMax.

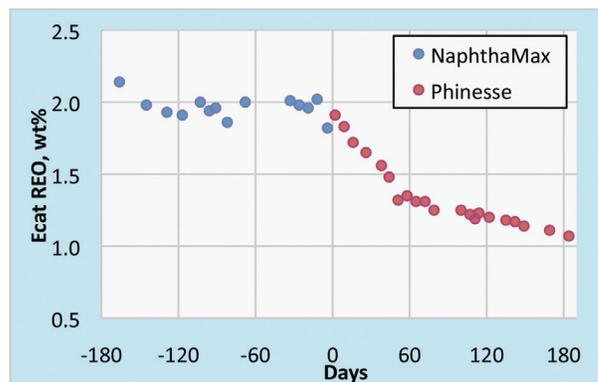
Based on the positive testing results, Phinisse entered the FCC unit in November 2012. The Ecat REO immediately started to decrease from 2 wt%, as shown in Figure 3. The unit was 75% turned over after three months, and essentially 100% turned over at six months. The metals showed an initial increase due to a feed change, and then proceeded to moderate.

Phinisse shows high activity stability. The catalyst held activity as well as the previous catalyst NaphthaMax at comparable metals and catalyst addition rates, even through the high metals excursion period (Figures 4 and 5). Despite Phinisse having half the RE, the stability is equivalent to the higher RE catalyst showing that the phosphorus modification effectively stabilises the zeolite.

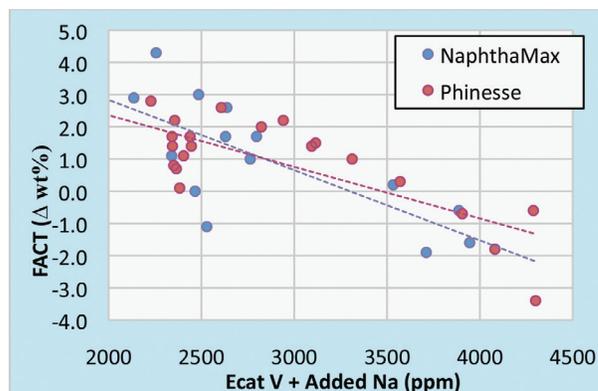
In addition to providing stabilisation of the zeolite, the phosphorus modification also provides selectivity shifts equivalent to that of RE modification. Phinisse gives the same gasoline selectivity with half the RE of NaphthaMax, as shown in Figure 6. This is a key proponent of the catalyst chemistry as units wishing to avoid the high cost of RE can switch to a lower RE catalyst and increase activity with high addition rates to offset the lower stability. However, the lower gasoline selectivity with lower RE catalyst (due to the lower H transfer) cannot be offset. Phinisse gives equivalent activity, stability and gasoline selectivity as NaphthaMax. Phinisse also gives higher LPG and LPG olefinicity than NaphthaMax (Figure 7).



**Figure 2.** Phinisse shows similar performance to NaphthaMax III with half the REO, and both show improved coke selectivity over NaphthaMax.



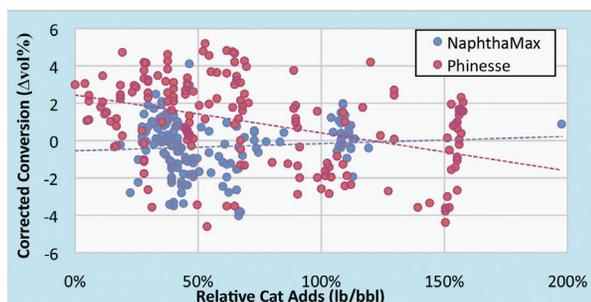
**Figure 3.** Ecat REO decreasing during the catalyst changeover.



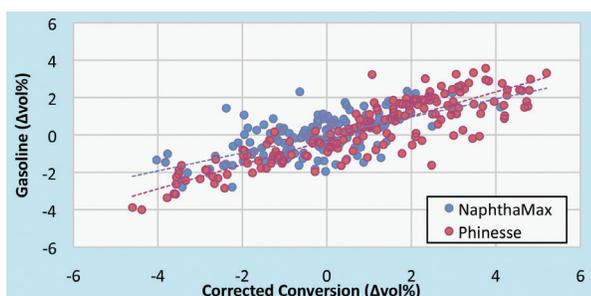
**Figure 4.** Relative Ecat activity versus Ecat V + added Na showing Phinisse and NaphthaMax have equivalent activity for the same contaminant V and Na level.

This is due to the improved coke selectivity of Phinisse resulting in higher cat to oil and higher LPG selectivity. With high olefin pricing, this was a desirable outcome.

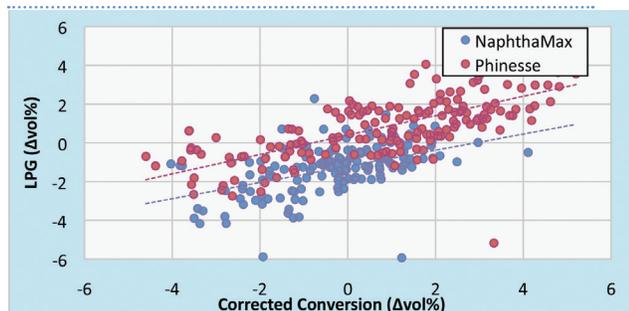
Phinisse also gave excellent LCO selectivity and bottoms upgrading (Figure 8). All unit operating data is confirmed



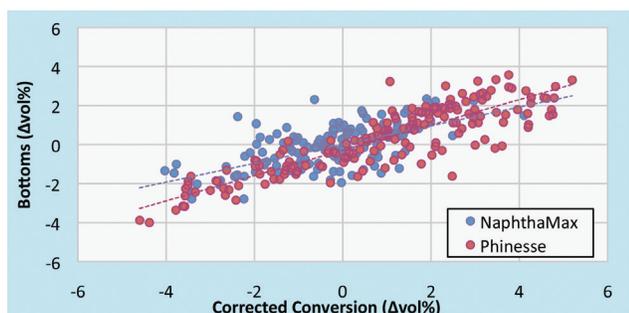
**Figure 5.** Corrected conversion versus relative catalyst addition rate showing similar activity retention for the time period.



**Figure 6.** Cut point corrected gasoline yield versus unit conversion showing NaphthaMax and Phinisse have the same gasoline selectivity.



**Figure 7.** Cut point corrected LPG yield versus unit conversion showing Phinisse has higher LPG yield as a result of the improved coke selectivity.



**Figure 8.** Cut point corrected bottoms versus conversion showing that NaphthaMax and Phinisse have the same bottoms selectivity.

with standard Ecat ACE testing throughout the trial showing that Phinisse gives equal performance for gasoline, LCO and bottoms selectivity along with improved coke selectivity.

The FCC unit saw no change in attrition with Phinisse. In addition, while using Phinisse, the unit underwent a restart. Upon resuming circulation, the Shell Sarnia FCC unit experienced lower losses with Phinisse than with the previous NaphthaMax catalyst.

## Post trial audit

Multiple post trial audits mimicking the refinery's operation of Phinisse confirm the commercial results. Ecats were tested using ACE, a circulating riser pilot plant, and Shell's riser pilot plant. Even though the price of RE had moderated back to historical levels by the end of the trial, Shell estimated the benefits of Phinisse, including improved coke selectivity and same gasoline selectivity as positive to make Phinisse economically viable.

## The path forward

BASF has introduced an innovative new FCC catalyst, Phinisse, using phosphorus based zeolite stabilisation chemistry. The chemistry uses phosphorus modification of the Y zeolite to achieve the stability and yield selectivity shifts of RE. Phinisse is designed using BASF's proven DMS NaphthaMax III catalyst technology for gas oil operation with lower RE and no performance debits. The first commercial trial at Shell Sarnia demonstrated that having half the RE (1 wt% versus 2 wt%), Phinisse gave the same high performance for gasoline, LCO and bottoms selectivity as NaphthaMax along with equivalent stability even through a metals excursion. As Phinisse is based upon NaphthaMax III technology, it also gave improved coke selectivity over NaphthaMax resulting in higher LPG and LPG olefins, which are highly valued. BASF continues research to enhance fundamental understanding of stabilisation, activity enhancement and selectivity shifts with rare earth alternatives. [\[1\]](#)

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