Active site developments for improved productivity

Developments including improved active site dispersion and assembly are designed for higher-valued operation in a range of processing units

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While global economies begin to show signs of recovery, refinery margins have continued to challenge even the most prescient planning and scheduling groups in our industry. As global/regional margins and demands fluctuate, and capital and operating budgets decline, the global drive towards clean fuels continues resolute, requiring refiners to squeeze the most from their existing units. In this environment, flexibility becomes one of the desired process capabilities to maximise refinery economics as margins continue to shift with feed and product slates. Given that overall unit performance is determined by capability, reliability and durability, technology providers are challenged to assist refiners to increase performance and flexibility without sacrificing run length.

In recent years, the ultra-low sulphur diesel (ULSD) unit has proven to be a versatile refining asset, demonstrating the ability to maximise diesel volume when margins are favourable and the flexibility to alter operations when the opportunities shift. However, the activity of many ULSD units is constrained, so higher-performance catalysts are required to unlock the full potential of the unit. With the reduction of cracking margins, FCC pre-treat operations have required the flexibility to shift from a role in maximum hydrogenation to a feed uplift service, enabling less valuable products to be shifted to clean fuels production. Increased catalyst activity combined with the ability to process difficult feeds with high levels of contaminants have produced economic value through improved run lengths and reduced generation of low-value products.

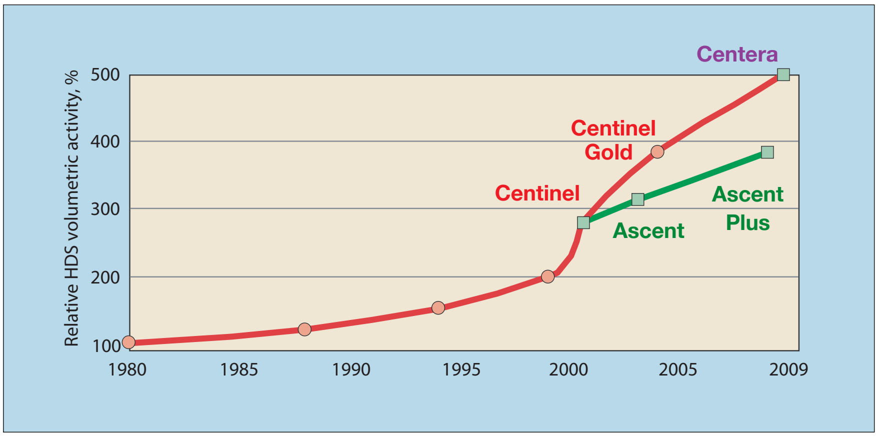

Figure 1 Relative performance comparisons

Criterion Catalysts & Technologies has developed Centera technology to meet the current challenges. In refining applications, including ULSD production, hydrocracker pre-treat (HCPT) and fluid catalytic cracker pre-treat (FCCPT), the product range has significant increases in activity and stability, and increasing unit capabilities to provide additional flexibility without sacrificing reliability.

Combined with customised catalyst system design, this technology can generate higher performance. Relative catalyst performance comparisons are shown in Figure 1. These solutions can improve overall refinery economics by providing the flexibility to process heavier feeds, maximise LCO blending into the diesel pool and/or extend unit cycle length.

Centera catalyst technology

The technology builds on elements of Criterion's Ascent and Centinel Gold developments and further increases performance through innovations in active site design and manufacturing technology. This combines improvements in catalyst support with advances in Type II active phases. Further advancements in the manufacture of Type II technology catalysts generate gains in both initial kinetic activity and enhanced retention of activity, resulting in a product range with the following characteristics:

- **Increased active site dispersion** Improved support technology leading to better dispersion of MoS_2 crystallites in the active catalyst
- **Maximum sulphidation** Manufacturing technology leading to the highest degree of sulphidation, forming ideal Type II active sites
- **Optimal assembly of active sites** Optimised decoration of MoS_2 edges with promoter metals leading to increased catalytic activity.

These conclusions are based on detailed characterisation of the active catalysts using various analytical techniques. The ability to perform molecular active site

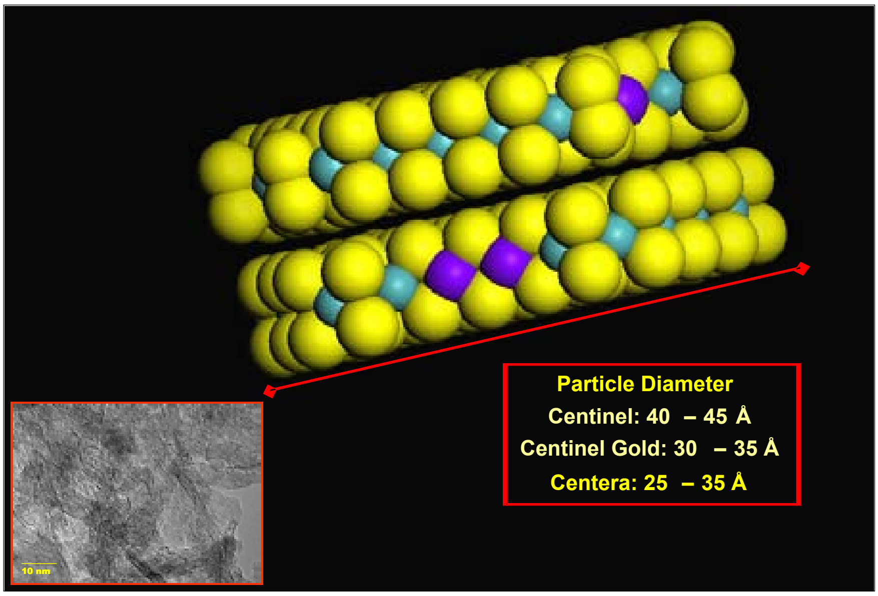

Figure 2 Molybdenum sulphide dispersion in Centera and Centinel catalysts

analysis and characterisation gives the framework for continued advances.

Increases in MoS_2 particle dispersion

Catalyst performance is a function of many parameters, one of which is metal particle interactions with the alumina support. Transmission electron microscopy (TEM) measurements and imagery can allow for detailed observation of particle formations of active metals and their dispersion on the alumina support. This observation and measurement provides the ability to further develop and optimise catalyst formulations and manufacturing protocols, both of which are key to the technology's performance.

During the development programme, a TEM protocol, specifically developed for characterising the catalyst, provided many digital images and measurements for each preparation, giving accurate analysis of metal sites.

During development, the quantification of dispersion of active metals sites was detailed with an observation of MoS_2 crystal slab lengths. Measurements of the slab lengths and the degree of stacking (layers) of the slabs were performed by examining hundreds of individual slabs per sample. Furthermore, the degree of stacking was determined by counting the number of layers in each individual supported particle of MoS_2.

A typical TEM image of the NiMo DN-3630 is shown in Figure 2. Evaluation of the image shows that the sample consists of supported (75%) and unsupported (25%) domains, each having particle sizes of around 35 Å. The average degree of stacking is 1.5 for the supported and 2.1 for the unsupported particles. An estimation of the particle size based on additional extended X-ray absorption fine structure (EXAFS) analysis leads to diameters of around 25 Å, indicating that the range given in the figure (25–35 Å) is a representative characterisation of the improvement seen with the technology when compared with earlier catalyst generation. The double-layered particle displayed in Figure 3 is thus a realistic description of the typical structure of sulphided DN-3630.

Maximised sulphidation with increased activity

The technology applies innovative manufacturing techniques to provide for complete sulphidation of the active metals. A critical element in achieving full sulphidation is to convert the Mo-O in the interior of the particle, thus minimising its interaction with the alumina support. Observations and measurements of the Mo-S structures within the active particles have been detailed utilising EXAFS spectroscopy. During the catalyst technology's development, EXAFS spectra of metals particles were obtained, to provide the Mo-S geometry and the extent of interactions with the support material. The inset in Figure 3 shows the Fourier transform of the respective X function from the sample. The first shell, at about 2 Å, is attributable to Mo-S contributions. It is identical to that of bulk MoS_2 and corresponds to the ideal coordination number of six, indicating that every Mo atom is surrounded by six sulphur atoms in trigonal prismatic fashion. Thus, the catalysts are fully sulphided with only weak van der Waals interactions with the support,

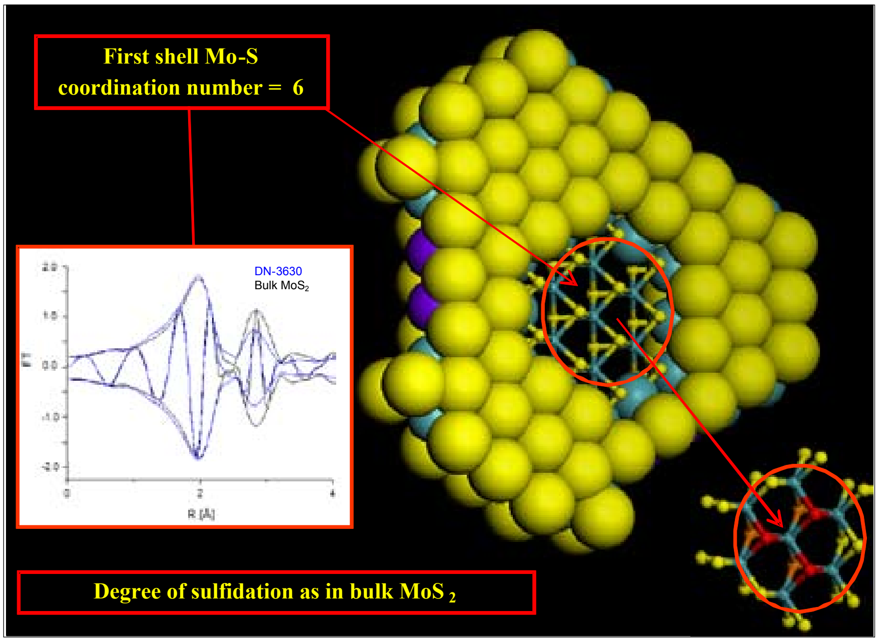

Figure 3 Full sulphidation of molybdenum

allowing maximum performance and complete utilisation of active metals.

Optimal use of promoter metals

An additional feature of the technology is the ability to "design" the active metals sites by influencing the placement of the promoter metals into the resultant Mo-Promoter Metal-S structure, allowing for enhanced performance of the active sites.

NO (nitric oxide) adsorption is a precise method used to characterise accessibility to the catalyst active sites and to determine the state of the sulphided catalyst Mo-S sites. The method is based on the observation that the N-O stretching vibration, as measured with Fourier transform infrared spectroscopy (FTIR), is structurally sensitive and enables discrimination between NO molecules adsorbed to Ni, Co or Mo. With Centera DN-3630, we can observe that the edge surface of a sulphided metals particle exposes only coordinatively unsaturated Ni centres. In this regard, DN-3630 displays unique surface structural properties. Molecular modelling calculations of different surface ensembles have shown that the active site edges have at least two, but possibly three, unsaturated promoter Ni centres in a row. It is the full presence of these specific active structures and the absence of less active, unsaturated Mo-based edge structures present in all other catalysts that is responsible for the increased activity observed with the catalysts. Figure 4 shows the differences in the edge structures of Ni-promoted Centera and Centinel catalysts.

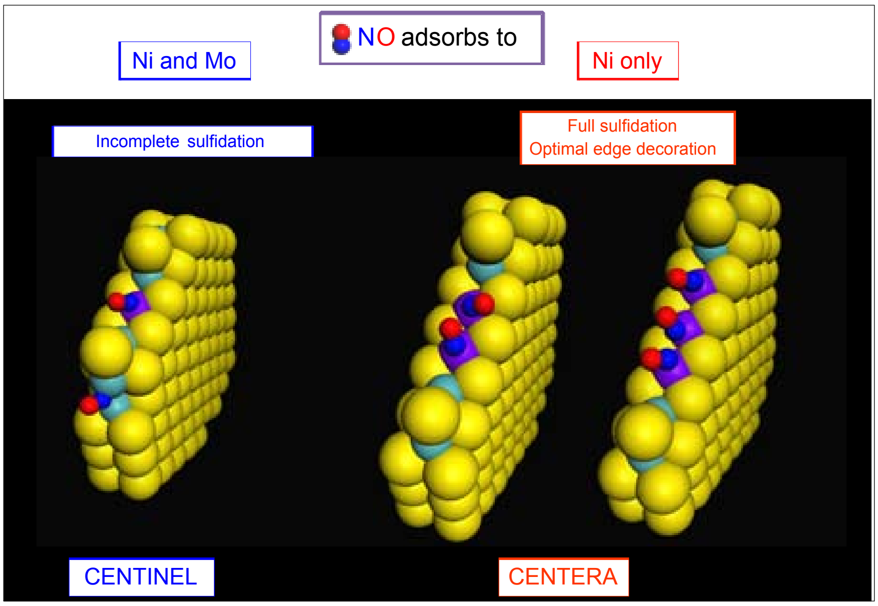

Figure 4 NO chemisorption: promoter edge decoration

FCC pre-treat gains

Centera was first introduced in ULSD service with DC-2618 and DN-3630, and its applications have been expanded into heavier feed applications, such as FCC pre-treat, with the initial release of DC-2650. DC-2650 was designed for enhanced HDS activity in low- to moderate-pressure VGO units, and is also combined with Ascent catalysts in a custom-designed catalyst system.

DC-2650 delivers significant gains for HDS targeted units, providing either extended cycle lives or reduced product sulphur for heavy VGO processing. When comparing previous generations of CoMo FCCPT products, the move from DC-200 to Centinel DC-2118 provided improved FCC feed quality via increased HDN, while the move to Ascent DC-2551 provided increased performance through increased contaminant uptake and reduced deactivation rates. Centera DC-2650 enables continued unit stability with gains in HDS capability. Figure 5 shows the relative performances of these catalysts.

Conclusion

With changing objectives and economics, catalyst systems have been developed to address the capabilities and the operational constraints of processing units.

The technology and manufacturing innovations applied in the initial Centera product releases have already shown capability for further gains in refinery performance. As development continues, additional product applications will service hydroprocessing needs in the refinery.

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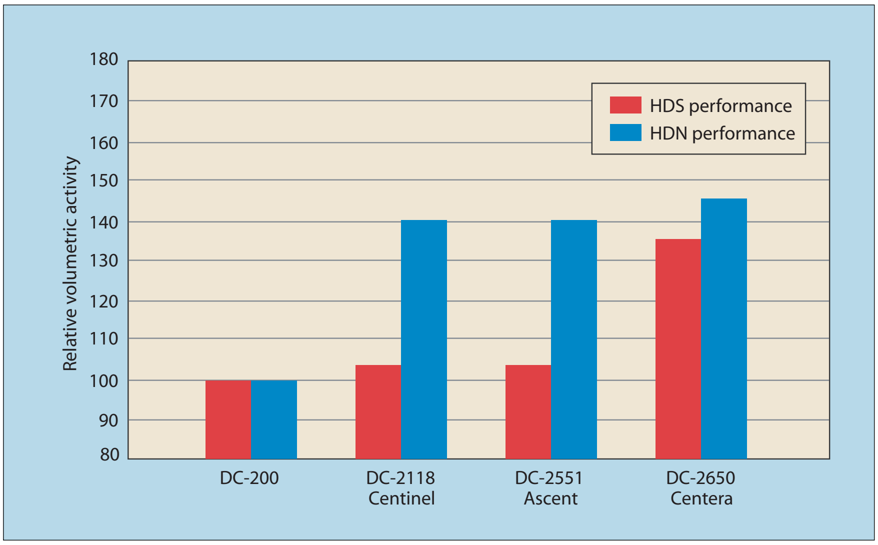

Figure 5 Relative performances of Criterion catalysts