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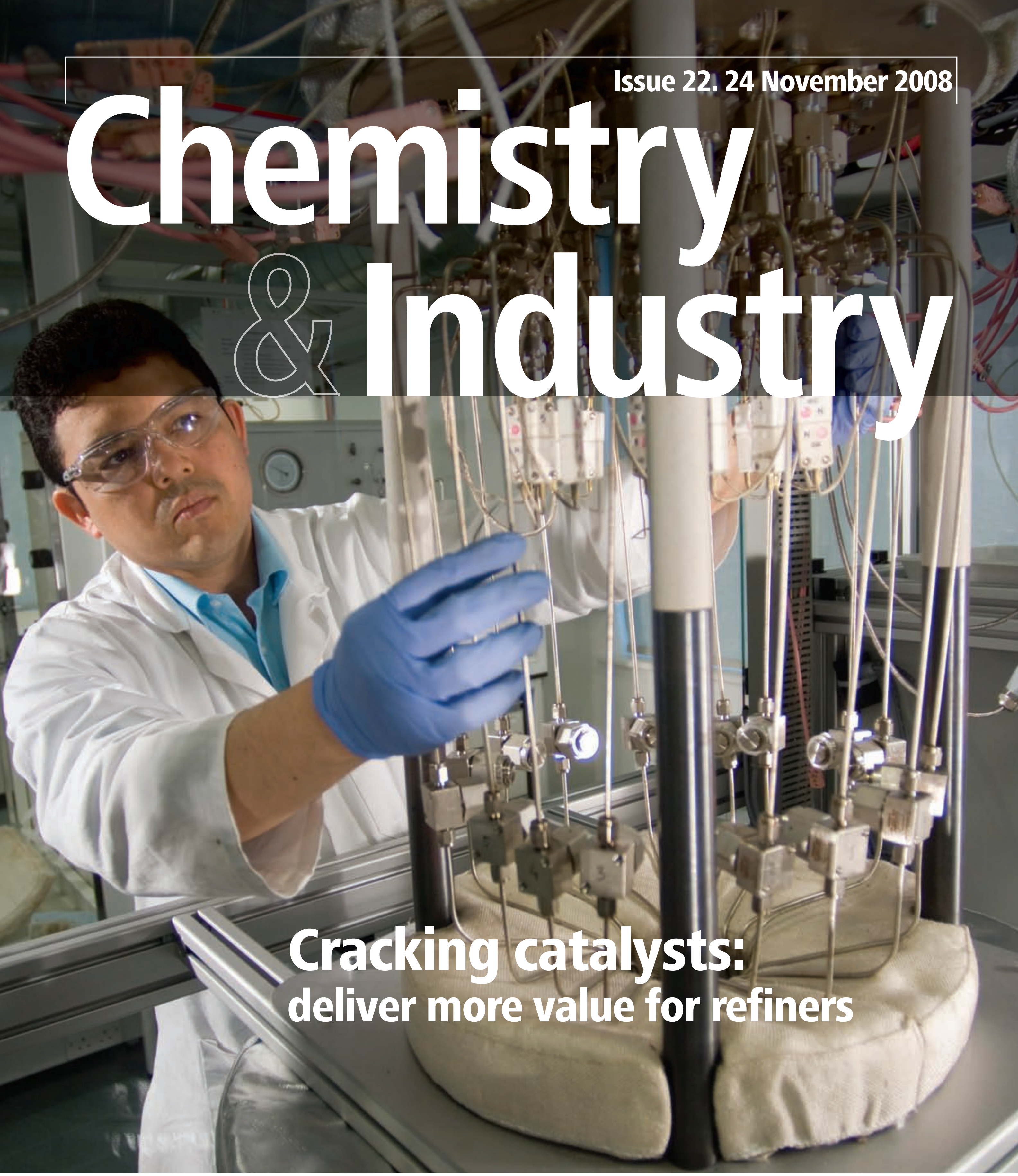

Cracking catalysts:
deliver more value for refiners

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Cracking the barrel

World reserves of crude oil are running out, but better catalysts promise to deliver more quality products from the remaining stocks, reports Cath O'Driscoll

According to the International Energy Agency (IEA), the demand for crude oil is expected to increase from 85m bbl/day in 2005 to roughly 115m bbl/day by 2030. But as existing supplies are used up, inevitably what is left – heavy and ultra-heavy oils and bitumen from tar sands – is poorer quality and harder to extract and refine. Apart from its higher density, non-conventional crude contains a higher proportion of foreign matter, especially sulphur and metals, which makes them harder to process.

'A catalyst acts as a product multiplier.'

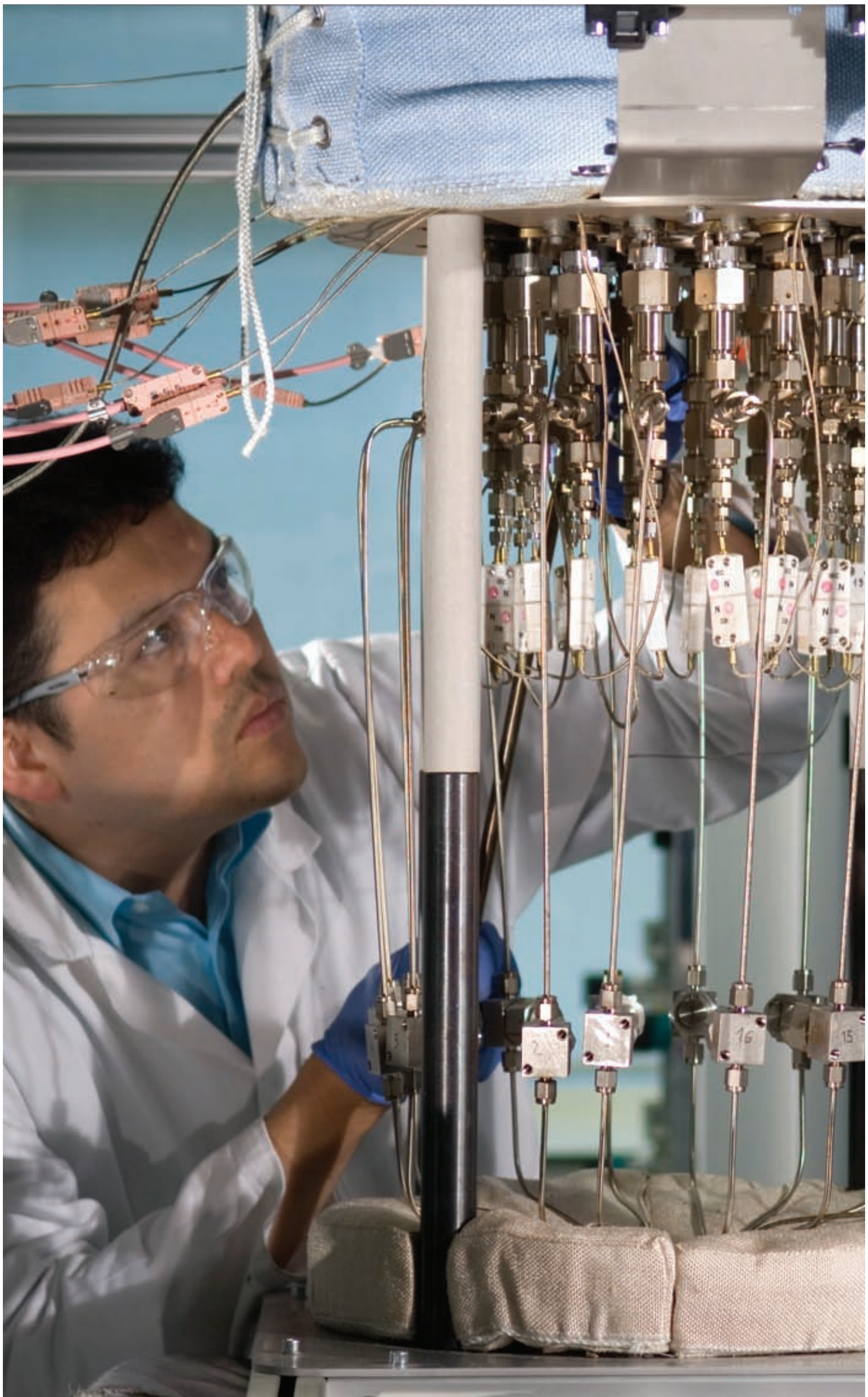
C. P. Kelkar,
BASF refining R&D manager

About 4bn t of crude oil are converted globally to petrochemicals every year. The two main processes responsible, hydrodesulfisation (HDS) and fluid catalytic cracking (FCC), convert 2bn and 700m t of petroleum to transportation fuel and valuable petrochemicals, respectively, making them the world's number one and two most important catalytic processes. According to figures

In Brief

- Heavy and ultra-heavy oils are poorer quality and harder to extract and refine
- Roughly 84mbbl of crude oil is refined per day, of which 28% is currently transformed to make diesel
- Diesel demand is expected to increase to 36% by 2020
- Propylene will see its share of the product slate rise from 1 to 3% by 2020
- Limited refinery capacities are another important driver for new catalyst development

Oxford catalysts



Oxford Catalysts

Loaded: refinery catalysts ready for testing from BASF, refinery catalysts account for $3.9bn of the overall $14.2bn market for heterogeneous catalysts, behind emission control ($6.2bn) and chemistry ($4.1bn) catalysts.

Catalysts able to convert poorer quality crude oil (naphtha) into more valuable products promise not only to extend the lifetime of crude, but also to increase profitability, says BASF refining R&D manager, C. P. Kelkar. A mid-size Fluid Catalytic Cracking (FCC) unit, for example, converts 50 000 bbl/day of petroleum to fuels and petrochemicals, he points out: 'A catalyst acts as a product multiplier.' For every 0.4% increase in desired product yield, that amounts to a $5000/day increase in profitability for manufacturers.

BASF has been supplying refinery catalysts to refineries, particularly for FCC processes, for over 35 years. In 2002, the group introduced what Kelkar describes as a 'breakout development' called *Distributed Matrix Structure* (*DMS*), a technology that he says took BASF to number one FCC catalyst supplier in North America. 'In FCC, the feed reacts over the catalyst for a very short time, from 2-5 seconds,' Kelkar says. 'Catalyst architecture has to be such that feed molecules can diffuse into the microsphere and products can diffuse out of the microsphere within that short timespan.'

The problem with earlier low pore volume catalysts, he explains, is that products became entrapped instead of diffusing out, and got converted to coke. Kelkar likens BASF's *DMS* catalysts to a 'house of cards' structure, with much higher pore volumes and improved poor volume distributions, resulting from the crystallisation of the constituent Y zeolites from the clay kaolin – produced by another BASF business unit as a filler for the paper industry.

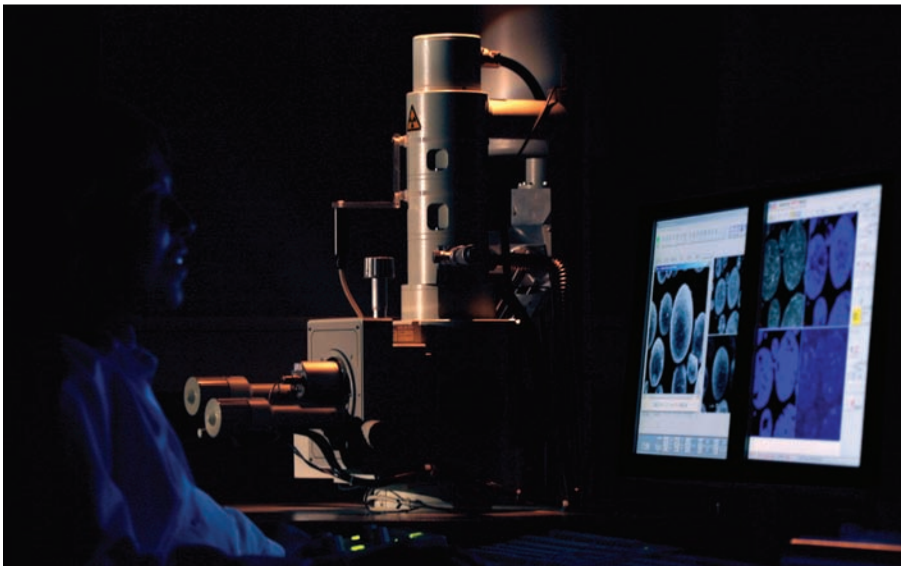
'In most cases a refiner switching either from older *in situ* or competitive catalyst to *DMS* technology saw more than a 2 volume% increase in conversion and a 2% increase in gasoline yield, resulting in significantly increased profitability,' Kelkar says.

The platform technology, which won BASF a Frost & Sullivan award in 2004, has now been expanded as a suite of catalysts including *NaphthaMax*, *Naphthaclean*, *Converter* and *Flex-Tec.*

Changes in the types of fuels being consumed, meanwhile, are also having an impact on catalyst performance. Of the 84mmbbl/day of crude oil refined, 28% of this is currently transformed to make diesel, but this is expected to increase to 36% by 2020 as higher fuel efficiency standards drive a trend towards using this as the fuel of choice for transportation.

Propylene likewise is expect to see its share rise from 1 to 3% of the product slate, as other products such as fuel oil see their share decline. In the coming year, BASF plans to test the performance a new FCC catalyst, designed to boost propylene output, in commercial refinery trials.

Experimental tests in the laboratory have already seen a 0.2-0.4wt % increase in propylene yield with the new catalyst, potentially increasing profitability of a 50 000bbl/day FCCU by up to $41 000/day, according to Kelkar.



Grace Davison

Surface analysis: **scanning microscopy of catalyst particles**

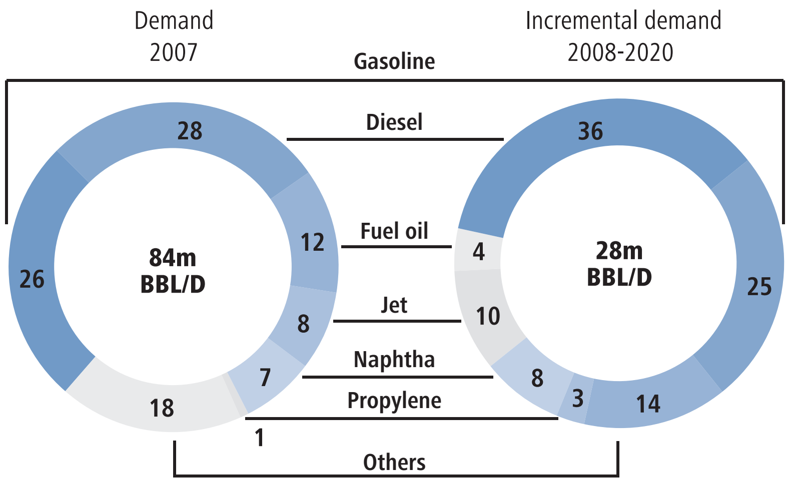
'What you see is a bigger difference in pricing between lighter and heavier grade feedstocks, with refiners seeing 10s of $/bbl difference in prices'

Troy DeSoto,
business director FCC Catalysts at Albemarle

At Grace Davison Refining Technologies Europe, researchers are working on a number of approaches to improve the processing of heavier feedstocks, also known as 'resid', says marketing manager Colin Baillie. Catalysts for resid processing need to have the ability to crack deep into the bottoms, he explains, which effectively means converting more of the less desirable Heavy Cycle Oils (HCO) into lighter, and more profitable, products.

An important catalyst requirement for resid applications is to limit coke formation, which inevitably accompanies the cracking. Reducing the yields of such by-product coke allows refiners to optimise the processing of heavier feedstocks while operating within the various constraints of the FCC unit hardware, such as regenerator temperature and air blower capacity. In addition,

Refined products demand



More propylene and diesel; less fuel oil
Source: Hart Energy Report/EIA report

protecting the catalysts from deactivation by metals poisoning is vital. Contaminant metals, such as nickel and vanadium, found in heavy feedstocks are problematic for two main reasons. First, they can deactivate the catalyst causing product yields in the FCC unit to deteriorate. Secondly, they can act as dehydrogenation catalysts resulting in the undesirable increase in hydrogen and coke yields.

Grace has developed a portfolio of resid catalyst families – *NOMUS, NEKTOR* and *NEKTOR-ULCC* – through its *EnhanceR* Technology Platform, which was introduced in 2003. Alumina-based matrices provide acid sites – where the cracking reactions take place – with the appropriate strength and density, as well as the pore structure for coke-selective bottoms cracking, Baillie says. These matrices also incorporate metals traps to passivate the contaminant metals found in the heavier feedstocks.

The firm has also designed a family of catalysts called *ProtAgon* to maximise FCC propylene yields. In contrast to the customary approach, using FCC catalysts in combination with additives, *ProtAgon* is an integral catalyst system. This eliminates catalyst dilution effects, retaining the high activity needed for increased propylene yields, Baillie elaborates. Recent testing at an unspecified Spanish refinery has shown that propylene yield could be increased from ca. 7.5 wt.% using a catalyst-additive combination to over 10 wt.% with *ProtAgon*. The refinery estimated that *ProtAgon* increased the FCC unit profitability by 7-9%.

The *EnhanceR* technology has also given rise to *NOMUS-DMAX* catalysts designed to maximise diesel output by preventing the 'overcracking' of the Light Crude Oil (LCO) from which this is derived. Increasing the catalyst pore volume enables a more-effective release of LCO molecules from the acid sites, Baillie explains.

The trend towards heavier crudes is also being driven even harder by price, notes Albemarle's Troy DeSoto, business director FCC Catalysts. 'What you see is a bigger difference in pricing between lighter and heavier grade feedstocks, with refiners seeing 10s of $/bbl difference in prices.' The challenge, he adds, is to process more resid as a percentage of the total so that heavier and heavier feed is turned into the same amount of valuable products, 'thereby dramatically improving the profitability of FCC'. This activity has to be maintained even in the face of large amounts of contaminants that destroy activity very quickly.

At Albemarle, researchers have developed what DeSoto says is a 'unique' measure of how readily molecules can enter and leave its catalysts after being transformed into products. Known as the *Albemarle Accessibility Index*, the approach is used to compare the activities and selectivities performance of the firm's own and other competitor catalysts. 'Yes, we see that our catalysts have the highest [accessibility indexes ratios]', he said.

Albemarle's *MD* catalysts line are intended to facilitate increased diesel production from FCC middle distillates (*MD*) and includes an *OPAL MD, CORAL MD, and UPGRADER MD*, useful for heavier feedstocks as well as *Upgrader MD*, *Coral MD*AMBER MD and *Ruby MD* for lighter feedstocks. also intended for increased diesel production. A further *AFX* catalyst is now available for maximising propylene output, and is currently being put to the test in a supply unit producing the world's largest yields of propylene, according to DeSoto.

As for how poor quality the possible feeds can go, DeSoto points to FCC feedstocks crude oils with so-called con carbon ratios up to 5-6 wt%; the 'ratio' refers to the amount of C left after everything else has been driven off via cracking and the higher the value the heavier and more intractable the starting feedstock crude. Conventional FCC feedstocks crudes typically have a con carbon ratio of 1-2 wt% for example.

Limited refinery capacities are yet another important driver for new catalyst development, according to Oxford Catalysts' Derek Atkinson – especially catalysts that can handle higher throughputs and run for longer. One of the biggest bottlenecks in most refineries, Atkinson points out, are the hydrotreating facilities used to remove sulphur and nitrogen oxides from the incoming feedstock prior to further processing. These facilities are increasingly needing to make much 'sweeter' products, with modern HDS units, for example, required to bring down sulphur levels from 5000ppm a few years ago to just 10ppm in the past few years. 'This is a bigger issue than you might anticipate as it becomes hard to find catalysts to remove sulphur below a certain level.'

Grace Division

ACE unit: to assess catalyst performance

Oxford Catalysts

***OMX* technology: catalysts ready to react**

'Our *OMX* technology allows us to produce catalysts that are significantly more stable and active than anything available elsewhere'

Derek Atkinson, Oxford Catalysts

Oxford Catalysts' *Organic Matrix Combustion* (*OMX*) technology controls the size of the metal crystallites of the active species in these catalysts, he explains. 'This increases the activity of the catalysts per gram of metal, resulting in both lower outlet impurity levels, as well as a greater total quantity of feedstock processed.' *OMX* technology, Atkinson claims, can improve the performance of all metal-based hydroprocessing (HDS and hydrodenitrification) catalysts independent of application.

One big advantage of *OMX* for HDS is the high activity of the resulting catalysts, he explains. The usual process to make nano-size catalyst particles requires water, but in the *OMX* procedure additional water is avoided by complexing the catalytic metal salt with urea. HDS and HDN processes currently use the largest quantities of supported metal catalysts, typically Ni, Co and Mo, he points out. 'The prices of these commodities have also fluctuated widely in recent years so whichever metal you choose you are still going to be at the mercies of the markets to some extent.'

A further advantage of the *OMX* technology is that the stability of the catalysts against deactivation, Atkinson says. It has been shown that very small metal crystallites are more prone to oxidation. The *OMX* technology, whilst reducing the mean crystallite size, actually results in a much narrower size distribution and hence virtually eliminates those very small metal particles.

However, higher activities are only part of the solution, Atkinson acknowledges. 'Our *OMX* technology allows us to produce catalysts that are significantly more stable and active than anything available elsewhere. For highly exothermic reactions, we can make catalysts that are far more active than any conventional reactor system can handle.' As well as the HDS catalysts, Oxford Catalysts has also applied its *OMX* technology to develop a range of catalysts for Fischer -Tropsch synthesis (*C&I* 2008, **10**, 11), and is currently working with suppliers of process intensified reactor systems that can handle the large amounts of heat generated with these very active catalysts.

'Our catalysts have been tested by a range of companies including some of the largest and almost exclusively the feedback has been positive. We expect to have demonstration plants producing tonnes of material next years and to be fully commercial for FT by 2010/2011.'