The severity of refining hydrotreating operations has been increasing steadily over the past decade as environmental regulations mandate more stringent specifications on refinery products, including gasoline, diesel and fuel oil. In addition, feedstocks have become more difficult, with higher levels of contaminants such as sulfur and nitrogen and higher levels of refractory components such as polycyclic aromatics. The demand for refined products has also grown, leading refiners to debottleneck existing units and increase throughput. This is particularly true for middle distillate production (diesel, heating oil, jet fuel, kerosene) where the global demand barrel is expected to increase by 10% by 2015, up from the current 35%.

Hydrotreating catalyst design
When designing a catalyst for a specific hydrotreating service, there are two key components, which need to be optimised: the support and the active metals. The catalyst support property...
which controls the number of active sites is surface area. As seen in the left side of Figure 1, the relative catalyst activity is a direct function of surface area. The next parameter to be considered is the level of active metals. Again in Figure 1, the relationship of metals loading and activity is given. As expected, activity increases with increasing metals level but not continuously. There is an optimum metals loading for each support. Catalyst activity will decrease if excess metals are added because they will begin to block pores.

Surface area is not the only support parameter that needs to be considered, pore size is equally important. For the catalyst to be active, the hydrocarbon reactants need to have access to the active sites. Consequently the pore size needs to be tailored to the boiling range of the feed stream. In the left side of Figure 2, there are two examples of this optimisation. Also in Figure 2 is the relationship of metals dispersion and activity. This represents catalysts with the same metals level but using different loading techniques to improve the dispersion of the metals and consequently the activity.

Figure 3 gives an example of the support optimisation process for a catalyst to be used in FCC pretreat service. The y-axis shows the relative activity of the different catalyst preparations and the x-axis from left to right represents increasing pore size. Pore size and surface area are dependent variables, as the pore size increases the surface area and thus the number of active sites decreases. On the left hand side the catalyst has a high surface area but the pores are too small to allow the large VGO molecules access to the active sites. On the right hand side, the pores are very large and allow easy access but the surface area is quite low. In both cases the activity is low. The optimum support has a pore size distribution, which minimises diffusion constraints and maximises the number of accessible active sites.

The ApART™ catalyst system
Using the above optimisation process, ICR 175, a NiMo catalyst and ICR 176, a CoMo, catalyst were developed for FCC pretreat service. Each type of catalyst has different performance characteristics. The NiMo catalyst has superior activity for hydrodenitrogenation, HDN, and aromatic ring saturation, HDA, while the CoMo catalyst is better for hydrosulfurisation, HDS. The other difference is the dependency on $H_2$ partial pressure for HDS; NiMo has a high dependency as it does for HDN and HDA, while the CoMo catalyst has a low dependency. These differences are important when considering the changing reaction environment with respect to $H_2$ partial pressure in a FCC pretreat reactor. The $H_2$ partial pressure drops as the reaction mixture flows down the reactor because of $H_2$ consumption and liquid vaporisation.

The primary functions of the FCC pretreater are removing organic nitrogen compounds and saturating aromatic rings to improve FCC conversion and gasoline yield and removing sulfur to improve the FCC product quality. The best way to accomplish this is to use a stacked bed catalyst system. This is the basis for the ApART catalyst system in which...
the ICR 175 is at the top of the reactor where the \( \text{H}_2 \) partial pressure is highest and maximum rates of HDN and aromatic ring saturation are achieved. At the bottom of the reactor where the \( \text{H}_2 \) partial pressure is lower ICR 176 provides superior HDS activity. As seen in Figure 4, the ApART system gives much better overall performance than the individual catalysts. Figure 5 demonstrates the advantage of this enhanced HDS activity as it leads directly to lower sulfur FCC gasoline and LCO.

Recently the ApART catalyst system has been improved with the development of ICR 309. This new formulation replaces ICR 176 and provides even better HDS and HDN activity. A comparison of the two systems and the ICR 175 reference are shown in Figure 6. This new system has been commercialised in a West Coast US refinery with excellent results. Figure 7 shows the actual and normalised data. The system is meeting all the predicted product targets and is extremely stable.

**ICR 179 catalyst**

Good HDN activity is critical for hydrocracking pretreat so that the downstream hydrocracking catalyst can operate most efficiently. ICR 179, which has recently been developed for this type of service, achieves improved HDN activity through a novel formulation, which increases Type 2 active catalytic sites. These sites have been shown to provide superior hydrogenation activity. Figure 8 shows pilot plant results on a Middle Eastern feed that has been denitrified to 1 ppm product nitrogen. ICR 179 demonstrates a significant activity advantage over the previous generation hydrocracking pretreat catalyst.

**Hydrocracking catalyst design**

The characteristics discussed above for good hydrotreating catalyst design, such as surface area, pore size, and metals loading and dispersion, also apply to formulating a good hydrocracking catalyst. In addition, hydrocracking catalysts contain an acidic function, which is responsible for catalysing the carbon-to-carbon bond breaking which is necessary for the production of lighter products. It is critical...
that the acid and hydrogenation functions are balanced, not only for efficient cracking but also to continue the hydrogenation process started by the pretreat catalyst. This is necessary to achieve the lower levels of sulfur, nitrogen and aromatics required for today’s (and the future’s) clean fuels.

CLG is continuing to build on Chevron’s 40 years of hydrocracking catalyst research and development and has recently been developing a new generation of hydrocracking catalysts. These improvements have come about by optimising the catalyst formulation including the proper choice of raw materials, improved characterisation, testing techniques, optimal synthesis steps and improved manufacturing processes.

Figure 9 shows that the current CLG base metal hydrocracking catalyst portfolio covers a wide range of applications. It is well established that catalyst selectivity generally decreases as activity is increased, the reason for which is discussed below. Selectivity in this chart refers to the relative yield of the desired product in a given application; diesel, jet, kerosene or naphtha. The goal of hydrocracking catalyst development is to push the selectivity curve up and to the right; i.e. increasing selectivity, activity, or both. Higher selectivity produces more of the desired product while higher activity allows the refiner to extend catalyst run lengths, increase throughput, or process more difficult feeds. The upper curve in Figure 9 shows the newer generation catalysts developed by CLG.

Figures 10 and 11 illustrate an example of how improved catalytic performance is achieved through modification of the acid function. These figures show the relative cracking rate constant as a function of carbon number for catalysts of varying activity. These curves were obtained by empirically fitting catalyst activity and selectivity data to CLG’s hydrocracking kinetic model.

Figure 10 shows that as activity is increased by increasing zeolite content or acid strength, the cracking rate constant for molecules in the middle distillate range increases faster than the general increase in rate constant through the entire boiling range of the VGO feed. Thus, the desired product molecules are preferentially adsorbed and overcracked, resulting in the selectivity decline shown in Figure 9. Figure 11 shows how the acidity function can be modified to reduce the amount of overcracking and result in a catalyst with higher activity while maintaining mid-distillate selectivity.
ICR 177 catalyst

The resulting performance data from the above discussion is shown in Figures 12 and 13, which compare the newly developed ICR 177 with CLG’s widely used ICR 142 mid-distillate hydrocracking catalyst. Figure 12 presents pilot plant data which shows a significant activity advantage of ICR 177 over ICR 142 as conversion is increased, while Figure 13 shows ICR 177 maintains selectivity at low to moderate conversion and actually improves selectivity at higher conversion.

New hydrocracking catalyst

Chevron has long been a leader in hydrotreating technology for lubricant base oil production. ICR 142 has long been the hydrocracking catalyst of choice for maximum VI of the unconverted oil. However, today’s increasing hydrocracking severity conditions tend to require more active catalysts. CLG is developing a higher activity catalyst with a novel formulation specifically designed for maximising VI. Figure 14 shows pilot plant data, which illustrates that the new catalyst is significantly more active than ICR 142 while Figure 15 shows comparable and even, improved VI of the unconverted oil at higher conversions. This catalyst is close to commercialisation.

ICR D210 catalyst

Hydrocracking catalysts for naphtha production generally require higher cracking activity than catalysts for mid-distillate production because of the increased C-C bond cleavage required to produce the lighter product slate. In general heavy naphtha is preferred over light naphtha (as reformer feed), and light gases have even lower product value. The challenge therefore is to design the acid function to minimise the overcracking of heavy naphtha to lighter products, similar to minimising the overcracking of mid-distillate as discussed above for mid-distillate selective catalysts. CLG has recently developed a new naphtha selective catalyst, ICR D210, which shows improved performance over CLG’s widely used ICR 210. This catalyst exhibits significantly improved performance for both activity and selectivity as shown in Table 1. Performance benefits are realised in both once-through and recycle mode.

ICR 240 catalyst

A schematic of CLG’s two stage hydrocracker design is shown in Figure 16. Gas oil conversion to products is conducted in two sequential stages. The first stage performs pretreat in the top beds followed by hydrocracking to moderate conversion (40 - 60 lv%) in the lower beds. First stage effluent is sent to a fractionator along with the effluent from the second stage. The fractionator bottoms is sent to the second stage were it is further cracked to full or partial conversion. Since the fractionator removes the H₂S and NH₃ produced in the first stage, the second stage operates in a ‘clean’ environment, which significantly enhances the kinetics thereby reducing the required reactor temperature and reactor size. In addition, the products from the second stage are of extremely high quality.
The proper formulation of the cracking catalyst is critical for optimum performance in the second stage reaction environment. Particular attention has to be paid to the acid function to minimize overcracking of the higher value products. For years, Chevron’s ICR 120 catalyst, an amorphous catalyst made by a proprietary cogellation technique, was the premier second stage catalyst in the industry for mid-distillate production. CLG has recently developed ICR 240, a mild zeolite new second stage catalyst to replace ICR 120. Commercial performance has exceeded expectations, with significant improvements in product selectivity as shown in Table 2.

In fact, the shift in product slate has been so dramatic that the refiner has reported very significant operational changes. ICR 240 has completely removed the light ends recovery bottleneck in the plant, which has allowed the refiner to increase throughput to 118% of design. The plant is now actually limited by its ability to recover mid-distillate! In addition, the impact from the hydrocracker has been so significant that total refinery throughput has increased several percent. The overwhelming success of ICR 240 is an excellent example of the large impact that a catalyst improvement can have on refining economics.

References