Introduction

Demands for a cleaner environment have led to more stringent global fuel specifications. The primary target has been a reduction in sulfur content. Currently on-road diesel fuel must contain no more than 10 parts per million by weight (wppm) sulfur in both the United States and the European Union. This standard also exists in a number of Asia Pacific countries. Because the production of ultra low sulfur fuels is primarily met by hydrotreating and hydrocracking, continuous improvement in catalyst technology is needed.

In 2001, Grace and Chevron combined resources to form Advanced Refining Technologies (ART) in order to provide world class hydrotreating catalyst technology to the refining industry. Chevron also has a long standing partnership with Lummus, a leading international engineering company, called Chevron Lummus Global LLC (CLG). ART and CLG offer a full product line of premium catalysts for upgrading products varying from heavy oil to distillates. Distillate hydrotreating operations include ultra low sulfur diesel (ULSD) and FCC and hydrocracker pretreat. Refiners, such as Chevron, use these catalysts to remove sulfur and other contaminants from petroleum to economically produce more environmentally friendly transportation fuels. As the most completely integrated source for hydroprocessing technologies and services, ART and CLG can provide incremental efficiencies at every step in a project.

This paper focuses on ART and CLG’s latest hydrocracker (HCR) pretreat catalyst development.

Hydrocracking Pretreat Catalyst Development

Good hydrodenitrogenation (HDN) activity is the primary function of the HCR pretreat catalyst because organic nitrogen compounds are detrimental to the performance of the HCR catalyst downstream. The rate limiting step in the HDN reaction pathway is aromatic ring saturation. This is because the most refractory nitrogen molecules are compounds like substituted carbazoles in which the nitrogen atom is incorporated into the aromatic ring at a fairly inaccessible position. The development of an improved catalyst therefore needs to focus on the catalyst properties that enhance ring saturation. The two critical components for optimizing catalyst performance are the support properties and active metals deposition technology as discussed in Reference 1.
Catalyst Support Development

Optimizing the catalyst support starts with the relationship between the physical structure of the support and the catalytic activity for the hydrocarbon stream being processed. Figure 1, from Reference 1, demonstrates this relationship.

The physical properties of the optimized support determine the maximum useful metal loading and consequently the maximum potential activity. Subsequent steps in the catalyst development process seek to utilize as much of this potential activity as possible. One aspect of this process is to look at the metal-surface interaction. Altering the alumina surface chemistry with inorganic additives can have a significant effect on active site formation and has been the subject of an ongoing investigation by ART and CLG scientists. ART’s 590DX has benefited from this study and utilizes a proprietary inorganic promoter to facilitate the formation of active sites during activation. An example of this work is shown in Figure 2.

Metals Deposition Technology

The current generation of HCR pretreat catalysts relies on the formation of DX active sites during manufacturing and activation to improve catalyst activity. The DX technology utilizes chelates to optimize metal function and consequently the activity and number of active sites.

The chelate binds preferentially to the transition metal ion, Ni, and controls the sequence of metal ion adsorption during the impregnation step. This allows the Mo to adsorb first, followed by Ni, and reduces the chance of the Ni interacting with the alumina support. The Ni associated with the alumina will ultimately form NiS which is inactive for HDN. During activation, the chelate delays the sulfidation of Ni relative to Mo. This allows the complete formation of the MoS2 slabs before the Ni ions are sulfided. Once Ni is released by the chelate during sulfidation it moves to the edges of the MoS2 slabs to form the highly active Type II sites.

There are many chelates available and they yield different performance benefits for the resulting catalyst. The ultimate choice is based on a combination of catalyst activity and manufacturing compatibility. Figure 3 demonstrates the impact of the chelating agent on catalyst performance.

FIGURE 1: Relationship Between Pore Size and HDN Activity for VGO

FIGURE 2: VGO HDN/HDS Performance of Catalysts With and Without Surface Modification

FIGURE 3: Chelating Agent Effect on HDN/HDS Performance of VGO
**ART 590DX Commercial Performance**

590DX was commercialized in the middle of 2009. By mid 2010 it had already been selected by seven refineries for catalyst refill. Figure 4 shows the HDN performance comparison between 590DX and the previous generation HCR pretreat, NDXi, in one of the Chevron refineries. 590DX is 20°F (11°C) more active than NDXi after 150 days on stream.

In one of the early uses of 590DX, there was an upset during the start-up which resulted in an extensive period without hydrogen flow. This compromised the start-of-run activity of 590DX. Despite the compromised start-up, the 590DX catalyst continued to activate, and became as active as the NDXi catalyst in the prior run at 2400 MBBLs on stream. Considering that the start-up of the prior run was not compromised, and that the feed in the prior run was less refractory than in the current run, it is clear that 590DX is a remarkably robust catalyst. The commercial results are summarized in Figure 5.

As a point of comparison, Figure 6 shows a different commercial operation for 2 cycles using the same catalyst grade. One cycle started-up normally while the other cycle had a significant upset during sulfiding. This data demonstrates a more typical result for a significant upset during start-up.

As can be seen in Figure 6, the major upset during start-up resulted in a significant permanent loss of activity and a much higher deactivation rate. This highlights the robust response of 590DX to operational upsets even during the critical start-up phase.

**Summary**

The formation of the ART joint venture in 2001 has resulted in a significantly increased rate of innovation for HCR pretreat catalysts as can be seen in Figure 7.

ART’s NDXi, 590DX and the prototype for 591DX are the catalysts in this series which utilize DX technology. NDXi is ART’s previous generation catalyst for HCR pretreat applications. The catalyst is also used in ULSD applications. It has been selected more than 40 times for catalyst refills and start-ups by many refineries since its commercialization in 2006. Many of the applications were selected through competitive pilot plant testing. NDXi has demonstrated a significant HDN activity advantage over the earlier generation catalyst, ART’s AT580. The base metal loading and alumina support is similar for AT580 and NDXi which confirms the advantage of chelate technology to more efficiently utilize the active metals.
ART is now commercializing 591DX, a wider pore version of 590DX, to handle VGO feeds with higher endpoints. The modified support properties will provide equivalent activity to 590DX but enhanced stability with heavier feeds.

**References**

1. Krenzke, Dave; Vislocky, Jim. *Hydrocarbon Engineering* (2007), 12(11), 57-58