ART introduced its line of ultra high activity DX™ Catalyst Platform in response to refiner’s demands for superior technology that delivers premium performance. This family of catalysts has exceeded expectations with its performance in demanding ULSD applications processing difficult feed blends. One of the keys to the ultra high activity observed with these catalysts is maximizing the utilization of active metals on the catalyst through ART’s chelate chemistry. This impregnation technology significantly improves metals utilization by allowing ART to manipulate the active metal components on the catalyst. It has been shown that when applied correctly chelates promote and enhance the formation of Type II metal sulfide sites (see Catalagram®, 96, 2004). ART CDX™ and NDX™ catalysts have demonstrated the benefits of this technology in ULSD units around the world both as stand alone catalysts and as part of a SmART Catalyst System® Series.

Building on this great success, ART’s dedicated research and development staff has recently announced the commercialization of its newest DX™ Catalyst Platform, 420DX. Figure 1 compares the activity of several generations of ART cobalt-molybdenum (CoMo) catalysts. The figure shows that 420DX offers 30% improvement in both HDS and HDN activity over CDX™ catalyst.
Researchers at ART have identified surface acidity as a key property for improved catalytic performance. It is generally accepted that there is a strong relationship between the role of increased surface acidity and improved reaction rate for reactions controlled through ring saturation such as nitrogen and hard sulfur removal. Changes in surface acidity have also been shown to affect the interaction of active metals with the alumina surface during impregnation. ART is able to exploit this phenomenon in the design of 420DX. This catalyst utilizes similar impregnation technology as CDXi where a chelate is used to bind to the cobalt ions in the impregnation solution and reduce interactions with the alumina support. The chelate/ion complex stays intact on the catalyst which allows the molybdenum to sulfide at lower temperature promoting the formation of Type II active sites.

With 420DX, this technology is enhanced through the use of a modified alumina carrier with improved surface acidity. This is demonstrated in Figure 2, which shows a pyridine infrared (IR) spectrum of the new support. The spectrum has a doublet at 1624 and 1616 wave numbers, as well as an absorption peak at 1452, which are thought to indicate the presence of Lewis acid sites. This confirms the incorporation of surface acidity in the new support. While the acid sites give 420DX better performance for both HDS and HDN activity, they are not strong enough to initiate any cracking reactions under typical hydrotreating conditions.

X-Ray Photoelectron Spectroscopy (XPS) was also used to help better understand the surface chemistry of 420DX. Figures 3 and 4 summarize some of these results. Figure 3 shows XPS spectra taken on a conventional (non-chelated) catalyst which has been sulfided at various temperatures. The spectra cover the binding energies for the expected Mo states with the MoS$_2$ state highlighted by the dotted red line at about 229 eV. The fresh catalyst
shows the presence of MoO₃ as expected. It is not until sulfiding 575°F that the MoS₂ peak becomes apparent. Figure 4 summarizes similar XPS spectra for a chelated catalysts like CDXi or 420DX. Notice in this case that the MoS₂ peak begins to appear at a sulfiding temperature of 260°F. This indicates that the presence of the chelate promotes sulfidation of the Mo at lower temperature compared to the non-chelated catalyst. Sulfiding the Mo at lower temperature results in a more fully sulfided Mo structure which promotes the stacking of the MoS₂ into Type II active sites. This explains much of the improved activity demonstrated by the DX™ Catalyst Platform.

To understand the improved activity of 420DX, one has to look at the Co species as a function of sulfiding temperature with XPS. Figure 5 summarizes these data for CDXi. The XPS spectra now show the binding energies characteristic of cobalt oxide (781-782 eV) and cobalt sulfide (778-779 eV). The binding energy for cobalt sulfide is highlighted in blue in the figure. The fresh catalyst shows the characteristic peak for cobalt oxide as expected. The cobalt sulfide peak becomes prominent for sulfiding at 575°F, but notice how broad the peak is for high temperature sulfiding. The wide peak indicates there are several states of cobalt present.

Figure 6 shows similar spectra for 420DX. Notice the much sharper peak for high temperature sulfiding for the cobalt sulfide species compared to the spectra for CDXi. This indicates that 420DX has a greater concentration of the active cobalt sulfide species which translates to higher activity.

ART has completed pilot plant testing over a variety of conditions to demonstrate the performance advantage of 420DX. Figure 7 shows the results of side-by-side testing of CDXi and 420DX at 980 psi hydrogen partial pressure and 2500 SCFB H₂/Oil ratio. At these
conditions, 420DX clearly outperforms CDXi by over 20°F at 10 ppm sulfur on a difficult feed containing 30% cracked stocks.

One of the additional benefits of 420DX is that the improved HDS and HDN activity has a minimal impact on increased aromatic saturation overall, and consequently does not increase hydrogen consumption to a measurable extent. This offers refiners greater flexibility in meeting their HDS activity requirements while minimizing hydrogen consumption using 420DX as a stand-alone catalyst or in combination with ART’s premium NDXi catalyst in a SmART System for producing ULSD from difficult feeds.

Additional pilot plant work was completed to look at the advantages of 420DX for moderate and high pressure applications using a SR feedstock. Figure 8 shows the expected SOR activity for seven ppm sulfur of 420DX and CDX. Note that again at higher pressure, 420DX shows a greater than 20°F improvement over CDX. At moderate pressure the activity difference is still greater than 10°F.

420DX will enable refiners to enhance their ULSD operation with either increased cycle length or additional use of opportunity feedstocks in order to maximize margin. Commercial samples of 420DX have been sent to several major oil companies with positive feedback that 420DX catalyst is a top tier product capable of exceeding refiners’ needs in demanding ULSD applications.