第 30 卷　第 8 期　　　催　化　学　报　　　2009 年 8 月
Vol. 30　No. 8　　　Chinese Journal of Catalysis　　　August 2009

文章编号: 0253-9837(2009)08-0836-03　　　综述: 836~838

加氢裂化预处理催化剂的发展

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摘要：讨论了雪佛龙技术转让部的加氢裂化预处理催化剂的发展历史. 用“更多的类型 II 活性位导致更好的 HDN/HDS 催化性能”理论解释了我们最近研发的加氢裂化预处理催化剂 HDN 催化性能好的原因.
关键词：加氢裂化; 预处理; ICR 179; ICR 511
中图分类号：O643　　　**文献标识码**：A

Hydrocracker Pretreat Catalyst Development

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Abstract: This paper reviews the history of Chevron Technology Marketing’s hydrocracker pretreat catalyst development. The excellent hydrodenitrogenation (HDN) performance on recently developed catalysts is explained by the theory that more Type II active sites lead to better HDN/HDS (hydrodesulfurization) performance.
Key words: hydrocracker; pretreat; ICR 179; ICR 511

The stringent legislation that has recently been enacted in many parts of the world requires very low levels of sulfur in fuels. Because of the urgent need to lower these sulfur levels, improvements in the industrial hydroprocessing process are needed. In order to synthesize highly efficient hydroprocessing catalysts, a deep understanding of the relationship between catalyst structure and catalytic activity is required [1].

Chevron Corporation and its Technology Marketing business (Chevron) have long been active in developing hydroprocessing technology. Chevron invented the modern hydrocracking process in 1959. The first licensed unit started up in 1962, and the first commercialized ISOCRACKING process within Chevron’s own system at the Pascagoula Refinery was implemented in 1963. Three years later, a two-stage ISOCRACKING plant was commissioned at its Richmond, California, refinery to upgrade vacuum gas oil (VGO) to naphtha and jet fuel. At the same time, a Single-Stage Once-Through (SSOT) unit was also commissioned at the Richmond Refinery to hydrocrack deasphalted oil (DAO). [2]

The researchers then found that the addition of a top layer of hydrotreating catalyst, a so-called “hydrocracker pretreat catalyst”, into an ISOCRACKING catalyst system can help to achieve longer catalyst life and higher catalytic activity [1].

Chevron, a leader and innovator in hydroprocessing technology, combined resources with the Davison division of Grace to form Advanced Refining Technologies (ART), and with Lummus, a leading international engineering company, to form Chevron Lummus Global LLC (CLG). ART and CLG offer a full product line of premium catalysts for upgrading heavy oil and for distillate hydrotreating operations, including vacuum gas oil, hydrocracking pretreat, and product post-treat applications. Refiners use these catalysts to remove sulfur and other contaminants from petroleum to produce more environmentally friendly transportation fuels. As the most completely integrated source for hydroprocessing technologies and services, ART and CLG can provide incremental

Received date: 9 April 2009.
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English edition available online at ScienceDirect (http://www.sciencedirect.com/science/journal/18722067).

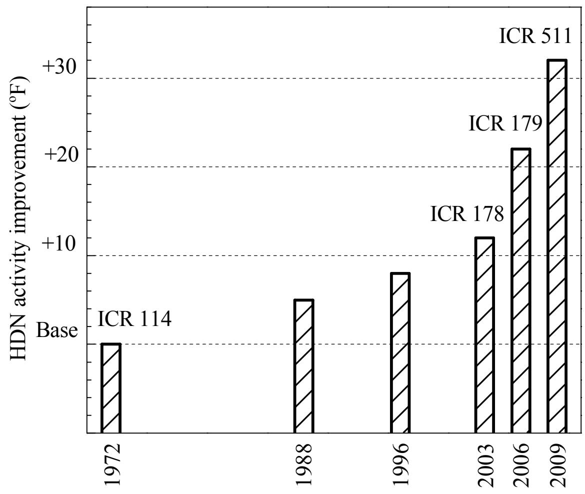

Fig. 1. Hydrocracker pretreat catalyst generations.

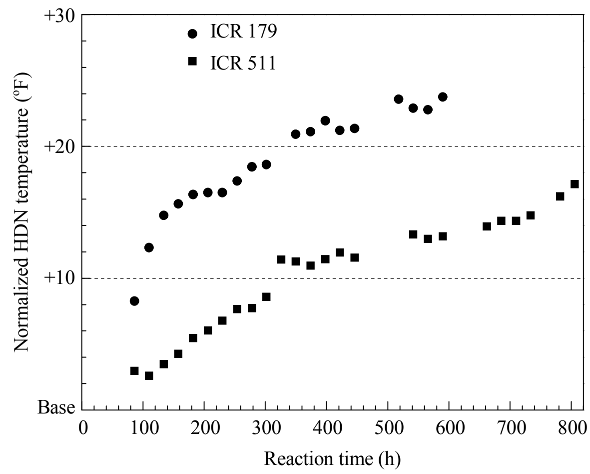

Fig. 2. VGO HDN activity in accelerated fouling test over ICR 179 and ICR 511. LHSV = 1.5, H_2/Oil ratio = 5000 scf/bbl, 0.1146% nitrogen feed (normalized to 10^{-6} nitrogen in the whole liquid product).

efficiencies at every step in a project.

The ART and CLG combination brings to bear hydroprocessing project planning skills honed from the completion of thousands of projects in more than 70 countries and balanced by the practical know-how that comes from hands-on, day-to-day operating experience in refineries. It is a range of experience that is unmatched in the industry, and it is available as a package or a set of individual services.

This paper focuses only on ART and CLG's hydrocracker pretreat catalyst development. Readers who are interested in the catalyst development of first-stage and second-stage hydrocracking are referred to the paper by our colleagues [2].

Good hydrodenitrogenation (HDN) activity is critical for hydrocracker pretreat, so the downstream hydrocracking (HCR) catalyst can operate most efficiently. In order to develop a better hydrocracker pretreat catalyst, a researcher needs to pay great attention to the relationship between HDN activity and catalyst structure. Apparently, active metals and support are two critical components for optimizing performance of a hydrocracker pretreat catalyst. The researchers in this field have accepted the theory that more Type II active sites will lead to better HDN/HDS performance [1].

Figure 1 summarizes CLG's hydrocracker pretreat catalyst generations. It is interesting to note that we have been able to develop new generation catalysts in a relatively shorter time since 2000.

ICR 179 is our current generation catalyst for hydrocracker pretreat and ULSD applications. The catalyst 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. ICR 179 has demonstrated a significant HDN activity advantage over the previous generation catalyst, ICR 178. This implies that there are more Type II active sites in ICR 179 than in ICR 178. It was achieved through changing the catalyst preparation route and thus changing the interaction between active sites and support.

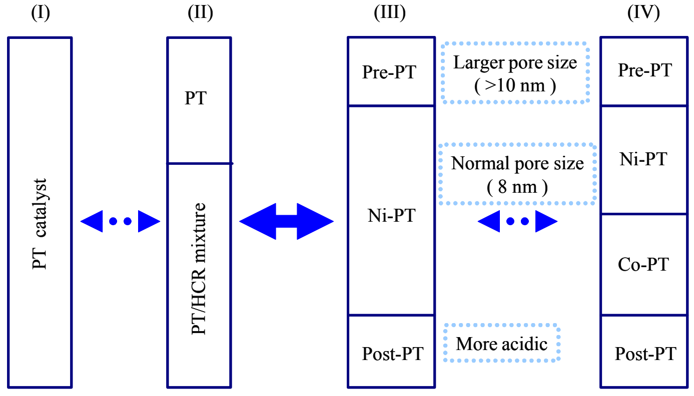

Fig. 3. Hydrocracker pretreat catalyst systems. PT: pretreat; HCR: hydrocracking.

Figure 2 shows HDN of a VGO with boiling point between 338 and 621 °C over ICR 179 and ICR 511. This VGO is a relatively tough VGO, which contains 0.1146% N and 2.7% S. It is clear that ICR 511 is more than 10 °F more active than ICR 179 for the HDN of this VGO. In fact, we observed that ICR 511 is more active than ICR 179 in a variety of VGO feeds. We achieved this improved HDN performance of ICR 511 by increasing the dispersion of Type II active sites. ICR 511 was commercialized in the second quarter of 2009.

Not only did we pay great attention to catalyst development, we have also tried to improve HDN performance by changing the catalyst system. Figure 3 presents four catalyst systems that are currently being applied in refineries. Compared with the second two systems, the first two systems are relatively old. By changing the catalyst system, we are able to satisfy requests from different refinery customers.

References

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