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Boron Based Technology for Fluid Catalytic Cracking and its Utilization in Refineries

Shaun S. Pan, Robert McGuire Jr., Gary M. Smith, and Bilge Yilmaz*

BASF Refining Catalysts, 25 Middlesex-Essex Turnpike, Iselin, NJ 08830 USA

*Corresponding author. Email: bilge.yilmaz@basf.com

Abstract

Resid feeds typically contain contaminant metals including Ni, V, Fe, and others. These metals catalyze a variety of unwanted secondary reactions. Being an especially active dehydrogenation catalyst, Ni presents a considerable challenge to refiners as it significantly increases H_2 and coke yields. Even small amounts of contaminant metals in the feed deposit cumulatively on the catalyst and can result in high H_2 and coke yields during FCC operation, which is a major concern for the refining industry. We have recently developed the Boron Based Technology (BBT), which is aimed at minimizing the negative impact of contaminant metals (especially nickel) as well as improving the selectivity to valuable products. The enhanced nickel tolerance is achieved by the boron compound loaded on a special inorganic support that is introduced into the catalyst. Combining this novel metals passivation functionality with a pore architecture that minimizes diffusional limitations of heavy feed molecules and enhanced acid site distribution, this new technology allows significantly lower hydrogen and coke yields coupled with higher make of valuable products. In this contribution an overview as well as specific examples on the development of this new technology will be provided.

Introduction

A significant portion of the FCC units around the world process feedstock containing residue (i.e. resid feeds). The tendency to process resid feeds is higher in parts of the world where access to light crudes is limited. Currently many units in South America process resid feeds. Resid feeds typically contain contaminant metals including nickel, vanadium, iron, and others. These metals catalyze a variety of unwanted secondary reactions (e.g., dehydrogenation). Being an especially active dehydrogenation catalyst, Ni presents a considerable challenge to refiners as it significantly increases hydrogen and coke yields. Even small amounts of contaminant metals in the feed deposit cumulatively on the catalyst and can result in high hydrogen and coke yields during FCC operation, which is a major concern for the refining industry.

Conventional Ni passivation techniques include the injection of antimony and the incorporation of Ni-trapping specialty alumina into the FCC catalyst. While antimony can be effective in reducing hydrogen and coke, it can also lead to increased NOx emissions and operational issues such as slurry heat exchanger fouling. The use of specialty aluminas for Ni-trapping also reduces hydrogen and coke. However, its efficacy is limited by the very low mobility of Ni. To better define intraparticle mobility of contaminant metals, a new method was developed [1] which utilizes scanning electron microscopy (SEM), Energy dispersive X-Ray spectroscopy (EDX) and/or Electron probe micro-analysis (EPMA) data of cross sectional areas of catalyst particles. Comparing the amount of contaminant metal on the outside versus on the inside gives the Peripheral Deposition Index (PDI) value [1, 2]. For Nickel, the measured PDI values are typically high, confirming its very low mobility [1, 2]. Ni is typically concentrated on the outer section of the Ecat, as a result of this low mobility under FCC conditions and it can be passivated only when it is in sufficient proximity to the alumina. The low mobility of nickel and alumina in the catalyst particle leads to insufficient passivation of Ni.

Boron-Based Technology (BBT)

A new technology named BBT (Boron Based Technology) has been developed recently [3] for resid applications where the negative impact of contaminant metals is minimized through the revolutionary boron based metals passivation approach. The enhanced metals tolerance is achieved by the boron compound loaded on a special inorganic support that is introduced into the catalyst. Combining this novel metals passivation functionality with a pore architecture that minimizes diffusional limitations of heavy feed molecules, this new technology allows lowest hydrogen and coke yields coupled with higher make of valued gasoline and light olefin products.

The key feature of BBT is the mobility of boron under the FCC conditions and the selective hunting for the un-passivated Ni. As a result, catalysts from the BBT platform are capable of achieving a much higher degree of Ni passivation than alumina-based Ni passivation technology. The BBT technology offers a variety of catalysts to refiners that are tailored for the metals passivation needs of their resid-FCC units (i.e., type/amount of contaminant metals etc.). Advanced cracking evaluation (ACE) results of a BBT catalyst loaded with 3000ppm Ni and 3000ppm V and deactivated following two different experimental procedures (CMDU and CPS-3) are presented below in Table 1 and Table 2 in comparison with Flex-Tec™ deactivated following the same procedures at the identical metals loading levels. ACE is a standardized testing method using a fixed fluidized bed, which simulates the riser performance. As shown in these tables, the catalyst from the BBT platform results in significantly lower hydrogen and coke yields, as well as higher activity and gasoline make compared to the base case. These findings demonstrate the enhanced metals tolerance and improved catalytic performance of the boron based technology compared to conventional metals passivation technologies.

Table 1: Advanced Cracking Evaluation (ACE) results at 75 Wt. % conversion; after cyclic metals deposition/deactivation (CMDU) with 3000ppm Ni, 3000ppm V.

ACE* Results	Flex-Tec	BBT
H_2	Base	- 27%
Gasoline + LCO	Base	+ 2%
Coke	Base	- 13%

Table 2: Advanced Cracking Evaluation (ACE) results at 75 Wt. % conversion; after cyclic propylene steaming (CPS-3) with 3000ppm Ni, 3000ppm V.

ACE* Results	Flex-Tec	BBT
H_2	Base	- 27%
Gasoline + LCO	Base	+0.75 %
Coke	Base	- 22%

FCC Unit Performance with Catalyst from Boron Based Technology

In this section we aim to give an overview of performance of catalysts from boron based technology in refinery trials. The example chosen here is from a commercial trial at a North American refinery. The refinery trial with the catalyst from the BBT platform was initiated in 2014. The FCC unit has a catalyst cooler and runs a moderate resid feed with 20-22 API gravity and 1-2% CCR. The main objectives for the unit are to minimize the amount of hydrogen produced as well as to maximize conversion and bottoms upgrading. The customer wanted to take advantage of the catalyst from the BBT platform to reduce the detrimental impact of nickel and improve operating flexibility and unit profitability. Prior to the BBT trial, the unit was using BASF’s Flex-Tec™ catalyst, which contains specialty alumina for Ni passivation.

Since this unit had been using purchased E-cat together with Flex-Tec™, during the trial the purchased E-cat usage pattern was maintained at a similar level to eliminate the contribution of purchased E-cat to the performance differences between the two catalysts. E-cat samples were supplied to BASF for physicochemical characterization as well as catalytic evaluation in ACE. All E-Cat samples were run under the same conditions (feed, temperature, catalyst-to-oil ratio etc.), in order to provide a good basis for comparison. In addition, samples of feedstock, FCC regenerator fines, slurry and scrubber water were sent to BASF laboratories for analysis in order to closely monitor the unit operation during the trial.

Equilibrium Catalyst Data Review

The Ecat equivalent Ni level, which is calculated by the standard Ni+V/4-4/3Sb formula, represents the equivalent dehydrogenation activity of the metals on E-cat samples. During the trial, the equivalent Ni level slightly decreased from 2700 ppm to 2500 ppm (Figure 1) and such a reduction was within the normal operating window for the unit.

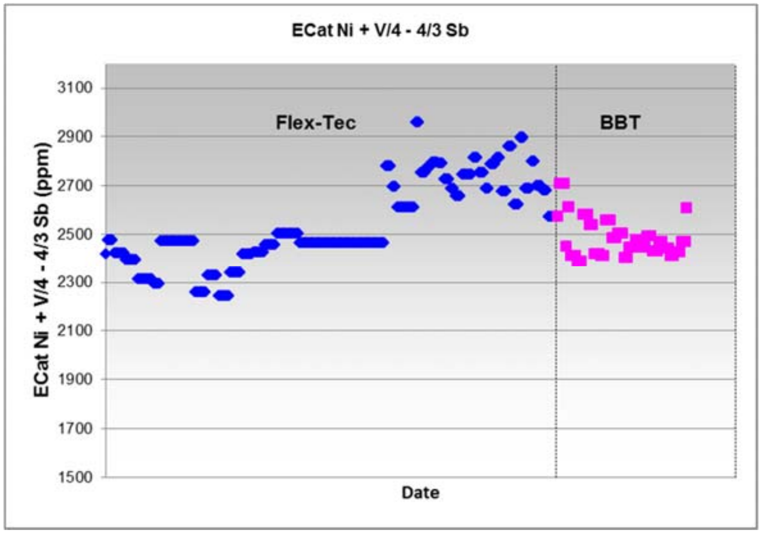

Figure 1: Equivalent Ni level on Ecat during Flex-tec and BBT periods.

The hydrogen to methane ratio (H2/C1) from ACE, which is typically considered an indicator of the hydrogen selectivity of the E-cat, was plotted against equivalent Ni level to compare the hydrogen selectivity between Flex-Tec and BBT samples. As shown in Figure 2, catalyst from the BBT platform reduced the H2/C1 by approximately 20% at constant equivalent Ni level at an inventory turnover of only 30%. The reduction in hydrogen make can be attributed to the passivation effect of the novel boron compound. Flex-Tec catalyst contains a specialty alumina, the conventional Ni trapping agent. As it was described in the introduction section, nickel has limited mobility under the FCC conditions, and thus a fraction of Ni cannot be effectively passivated by the stationary alumina as this conventional approach of "trapping" relies on the Ni-containing hydrocarbon molecules to crack at locations with close proximity to a trapping specialty alumina crystal to be taken up by that framework to hinder its dehydrogenation activity. The novel boron compound used in boron based technology is loaded on a proprietary inorganic oxide matrix which gets activated under the hydrothermal conditions of the FCC operation and triggers the controlled release mechanism. The passivating boron compound is mobile within the FCC catalyst. This mobility enables the boron compound to actively hunt for and passivate Ni molecules and thus reduce the overall dehydrogenation activity of Ni. One significant advantage of the boron-based Ni-passivation concept is that the freshest Ni, which is most detrimental in terms of its dehydrogenation activity due to its well-dispersed nature, is also the most accessible for passivation via BBT. The passivating boron compound can swiftly interact with these active and accessible Ni molecules, which would have the highest dehydrogenation activity, leading to a much more rapid passivation. Thus, BBT results in a more substantial and rapid reduction in E-cat hydrogen than Flex-Tec even at low change-over levels.

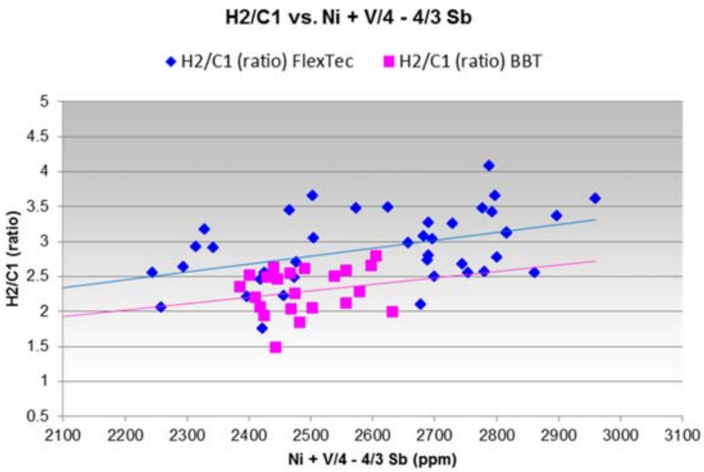

Figure 2: H2/C1 (ACE) vs. Equivalent Ni level for Flex-Tec and BBT equilibrium catalysts.

Enhanced nickel passivation by boron based technology also leads to a significant improvement in coke selectivity. Figure 3 shows the fluidized coke factor (coke yield adjusted for activity, an indication of coke making tendency of a catalyst) calculated from ACE as a function of the equivalent Ni. BBT catalyst lead to a lower FCF at constant equivalent Ni. Such an improvement in coke selectivity can be attributed to the nickel passivation by the boron compound. The passivating boron compound can reduce the detrimental dehydrogenation activity of Ni and thus the contaminant coke yield. The refinery can further realize additional benefit from the improved coke selectivity by being able to lower the regenerator temperature of the unit, thus increasing the catalyst-to-oil ratio and the unit liquid yields.

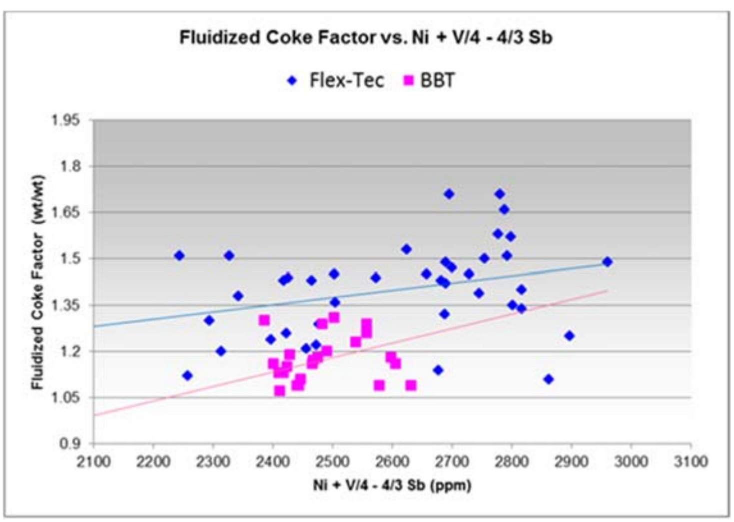

Figure 3: Fluidized coke factor (ACE) vs. equivalent Ni for Flex-Tec and BBT equilibrium catalysts.

Operating Data Review

The significant impact of boron based technology in reducing hydrogen yields was also observed in the unit operating data. As shown in Figure 4, the hydrogen-to-methane ratio in the operating data, an indication of hydrogen selectivity in the unit, was plotted against equivalent Ni level of the equilibrium catalyst. BBT period showed a ~25% lower H2/C1 ratio compared to the Flex-Tec period. The reduction in hydrogen again demonstrated the improved Ni passivation efficacy of boron based technology in Ni passivation and in reduction of the dehydrogenation activity in the unit.

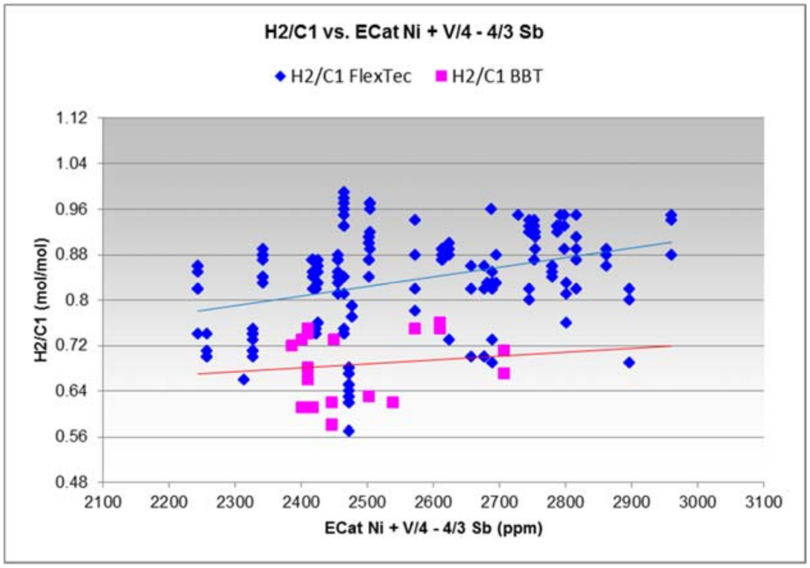

Figure 4: Operating H2/C1 ratio vs. Ecat equivalent Ni ratio for Flex-Tec and BBT catalysts.

To normalize the operating conditions and demonstrate the yield and profitability improvements delivered by boron based technology, KBC FCC-SIM modeling was utilized. As shown in Table 3, at constant operating conditions, the new catalyst decreased the operating delta coke through more effective passivation of contaminant metals, which lead to a significant reduction in contaminant coke. The reduction of contaminant coke allowed a higher catalyst-to-oil ratio to be run in the FCC unit leading to a higher unit conversion. The unit hydrogen make decreased by a third from 0.15 wt.% to 0.1 wt.% and bottoms yield decreased by 0.3 vol%. Gasoline and LPG yields increased by 0.5 vol.% and 0.9 vol.%, respectively. As a result, the FCC unit profitability improvement was calculated to be \$0.32/bbl in the winter time and \$0.38/bbl in the summer time, based on the seasonal economics.

Table 3: Projected unit yields for Flex-Tec and BBT catalysts at constant operating conditions.

	Flex-Tec	BBT	Delta
Delta coke (wt/wt)	0.71	0.64	-0.07
Conversion, wt.%	69.0	69.4	+0.4
H2, wt.%	0.15	0.10	-0.05
LPG, vol.%	27.8	28.7	+0.9
Gasoline, vol%	52.5	53.0	+0.5
LCO, vol.%	12.1	12.0	-0.1
Bottoms, vol.%	7.7	7.4	-0.1

Conclusions

Boron Based Technology (BBT), the new catalyst technology platform developed by BASF for resid applications, is aimed at minimizing the negative impact of contaminant metals (especially nickel). The enhanced nickel tolerance is achieved by the boron compound loaded on a special inorganic support that is introduced into the catalyst. Combining this novel metals passivation functionality with a pore architecture that minimizes diffusional limitations of heavy feed molecules, this new technology allows lowest hydrogen and coke yields coupled with higher make of valuable hydrocarbon products. The BBT technology platform offers a variety of catalysts to refiners that are tailored for the metals passivation needs of their resid-FCC units. In this contribution, performance of a catalyst from the BBT platform in a commercial FCC unit was described in detail and compared to the performance of the previous catalyst in the unit (Flex-Tec) that utilizes a traditional specialty alumina based Ni-trapping technology. Use of the BBT catalyst in the refinery resulted in significantly lower hydrogen and coke yields and improved unit economics. The experimental studies as well as the operating data collected during the refinery trial demonstrate the enhanced metals tolerance and improved catalytic performance of the BBT platform compared to conventional metals passivation technologies.

References

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CV:

Bilge Yilmaz, Global Technology Manager, BASF Refining Catalysts

Ph.D. Chemical Engineering – Northeastern University, Boston, MA, USA

M.S. Chemical Engineering – Northeastern University, Boston, MA, USA

B.S. Chemical Engineering – Middle East Technical University, Ankara, Turkey