Optimising refinery margins with rejuvenated catalysts

Rejuvenated catalysts compare well with fresh catalyst for performance and stability, with added cost savings

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Across the world, lower growth in demand for fuels in recent years, weak profit margins, strict environmental regulations on CO_2 emissions and legislations in different countries for renewable fuels are making a major impact on the refining industry. In this scenario, there is a greater need to optimise the refining costs and maximise profitability.

Catalyst replacement after completion of its lifetime in a reactor for different applications is an important expenditure in a refinery and can be optimised by wise selection of appropriate catalyst. Excel rejuvenated hydroprocessing catalyst from Evonik is one candidate for ultra-low sulphur diesel (ULSD) application which can help refiners to reduce operating costs and maximise profitability while remaining environmentally conscious with their hydroprocessing applications.

What are rejuvenated catalysts?

In a diesel hydrotreatment reactor (ULSD application), catalysts are replaced typically after an interval of four years. ULSD catalysts deactivate mainly due to coke deposition over their lifetime. To recover the activity of the catalyst, coke is removed by carefully burning it under mild oxidative conditions. This is typically referred to as regeneration. In this process of coke removal the active sites over the catalyst may sinter or agglomerate due to exotherms. The selective removal of metal contaminant deposits and restoring near to fresh activity of spent catalyst is achieved by rejuvenation.[1] Excel rejuvenation enables redispersing agglomerates on the regenerated material to restore its activity to near fresh by utilising a proprietary chemical treatment.

Feed to diesel hydrotreater used to perform catalyst testing

Analysis	Feed to diesel hydrotreater
Density 15°C, kg/l	0.8637
Sulphur, wt%	0.51
Nitrogen, ppm	365
Bromine number, g/100 g	2.70
Total aromatics, wt%	34.8
Simulated distillation (ASTM D 2887)	
10 wt%, °C	230
95 wt%, °C	390

Table 1

Evonik's solutions achieve benefits such as:

- Reduction of the catalyst refill cost by about 50% compared to fresh catalyst
- Faster catalyst supply compared to long lead time for fresh catalysts
- Better environmental footprint since these hydroprocessing solutions decrease CO_2 emissions and avoid catalyst waste to landfill
- Similar performance compared to fresh catalyst in terms of activity and, more importantly, in terms of stability

By using rejuvenated catalysts, CO_2 emissions will be reduced, by comparison with fresh catalyst production, by approximately 6000 kg CO_2/t of fresh catalyst replaced and thus contribute significantly to circular economy. Over the last five years, Evonik has supplied more than 7000 tons of Excel rejuvenated catalyst to refineries worldwide, resulting in reduced emissions of 42 000 tonnes of CO_2.

To demonstrate the robustness of Excel rejuvenated catalysts, independent catalyst testing and comparison was performed at Q8 Research. In this study, three fresh ULSD catalysts from different catalyst vendors were compared with their respective Excel rejuvenated catalysts. Moreover, commercial data comparing rejuvenated NiMo and fresh NiMo is compared to illustrate the stability of the Excel catalysts.

Experimental

A parallel high throughput reactor unit was used to compare the performance of the catalysts.[2] The catalyst testing was performed at multiple temperatures at the same pressure, hydrogen to oil ratio, liquid hourly space velocity (LHSV), and hydrogen purity.

The feed from a European refinery diesel hydrotreater was used to perform catalyst testing (see **Table 1**). The experiments were performed at hydrogen partial pressure of 50 barg, LHSV = 1.45 h^{-1} and H_2/oil = 160 Nm^3/m^3.

A common wetting and activation/sulphiding procedure was implemented. Dimethyl disulphide (DMDS) was added (3.67 wt%) to straight run gasoil for the catalyst sulphidation/activation. Catalyst activation was followed by line out period and start of run (SOR) temperature conditions. The experiments were designed in such a way that sulphur effluent at different conditions ranged between 10 ppm and 150 ppm. The results for fresh CoMo and their respective Excel rejuvenated CoMo catalysts (see **Table 2**) were modelled using a pseudo first order kinetic plug flow reactor model. The apparent first order rate

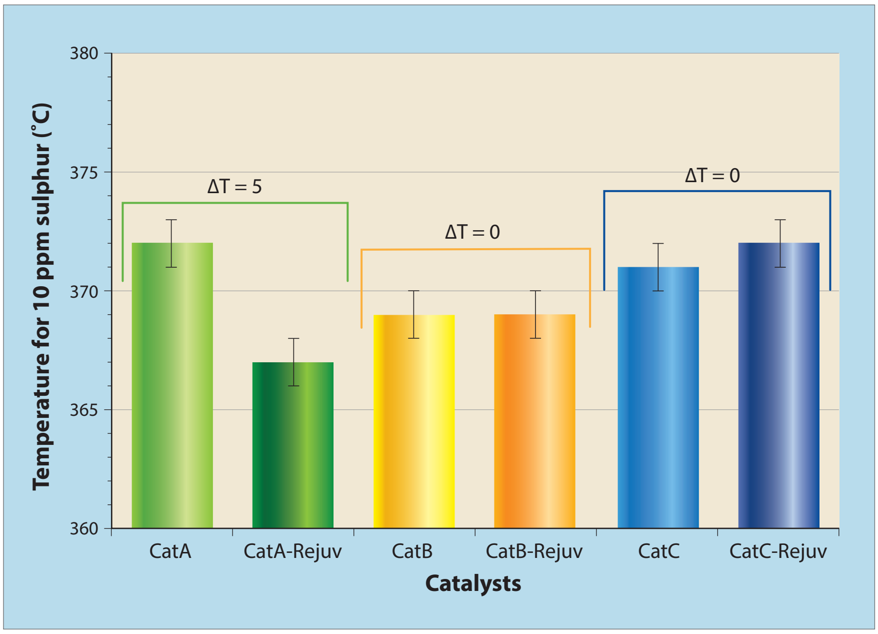

Figure 1 Activity comparison of fresh and Excel rejuvenated commercial ULSD catalysts

Commercial CoMo catalysts used for catalyst testing

Vendor	Fresh catalyst	Excel rejuvenated catalyst
1	CatA	CatA-Rejuv
2	CatB	CatB-Rejuv
3	CatC	CatC-Rejuv

Table 2

Feed and operating conditions of a European refiner

Parameter	ULSD mode	Heating oil mode
Feed sulphur, wt%	0.29	0.44
Feed nitrogen, wtppm	250-350	400-500
Density, kg/m^3	850	867
D-86 (FBP), °C	360	381
Operating pressure, barg	71	71
LHSV, h^{-1}	3.1	2.6

Table 3

constant (see **Equation 1**) for the catalysts at different temperatures was calculated and used to develop the kinetic model for each catalyst:

$$k\,(T) = LHSV\left[ln\left(\frac{C_{feed}}{C^{(T)}_{effluent}}\right)\right] \quad [1]$$

where k(T) is the apparent first order reaction rate constant, C_{feed} is the sulphur concentration in the feed, LHSV is the liquid hourly space velocity and $C^{T}_{effluent}$ is the concentration of sulphur in the effluent at T temperature.

Results and discussion

The catalysts (see **Table 2**) were tested in parallel for about 30 days time-on-stream at various process conditions. The HDS activity of the fresh catalysts was compared with the rejuvenated catalysts. In the case of type B and type C catalysts, the rejuvenated ULSD catalyst had similar activity compared to fresh catalysts. In the case of type A catalyst, the rejuvenated catalyst was even more active compared to the fresh catalyst. This implies that not only the catalyst activity was recovered in most of the rejuvenated catalysts but in some cases it is better than the fresh catalyst. This is possible as, due to chemical treatment, it can enhance the redispersion of the active sites which are originally present in a fresh catalyst. The activity comparison is performed by use of kinetic modelling to determine the temperature needed to achieve 10 ppm sulphur in each catalyst. The rejuvenated catalyst of type A (CatA-Rejuv) was 5°C better in activity compared to the activity of fresh catalyst (see **Figure 1**). In the cases of type B and type C catalyst, the HDS activity was similar for fresh and rejuvenated catalyst (see **Figure 1**).

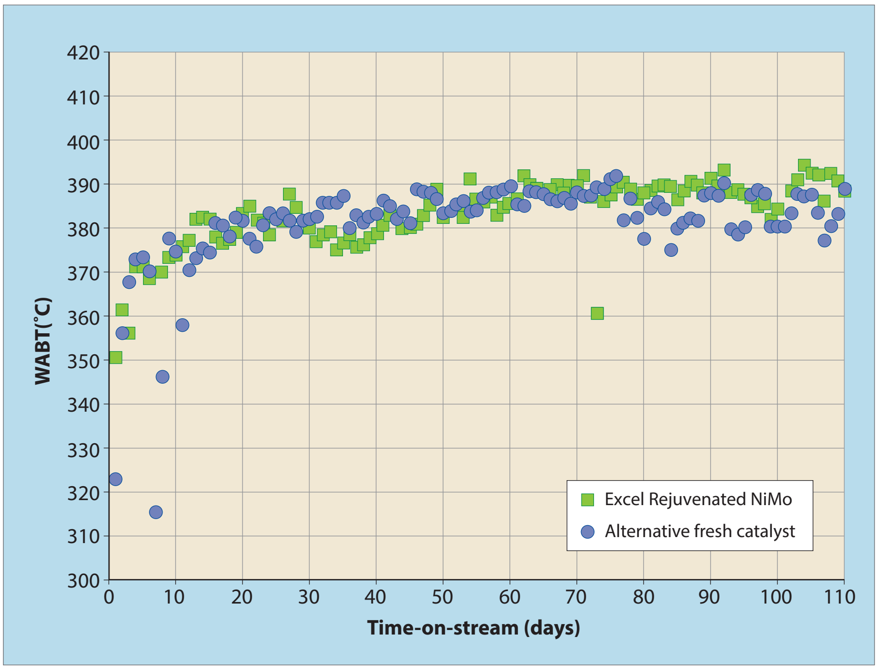

Figure 2 Comparison of Excel rejuvenation with conventional fresh catalyst

Example of commercial run

Evonik installed a high activity Excel rejuvenated NiMo catalyst to help a refinery extend the hydroprocessing unit cycle until the next turnaround.[3] The catalyst was proposed to maximise HDS/HDN activity and polyaromatics hydrogenation. The feed and operating conditions were carefully evaluated to optimise catalyst system design and simultaneously meet multiple unit objectives. Throughout the technical evaluation, there was a commitment to ensure high catalyst quality to maximise performance and reliability. The European refiner operated the diesel hydrotreater (DHT) unit in two modes:

- ULSD mode by processing a blend of light gasoil (75 wt%), heavy gasoil (3 wt%), vacuum gasoil (2 wt%), and cracked gasoil (20 wt%)
- Heating oil mode by processing a blend of light gasoil (20 wt%), heavy gasoil (45 wt%), vacuum gasoil (15 wt%), and cracked gasoil (20 wt%)

As a result, the unit was able to process a blend of light and vacuum gasoil with coker distillate to produce two grades of final product. The unit achieved the projected cycle length while reducing catalyst expense. A summary of the feed and operating conditions is shown in **Table 3**.

The Excel rejuvenated NiMo catalyst provided high HDN activity combined with deep HDS levels to handle the high nitrogen concentration in the feed blends. The primary objectives of the hydrotreater were:

- To produce ULSD, targeting a product sulphur of 11 wtppm
- To produce heating oil, targeting a product sulphur of 55 wtppm

Rejuvenated catalyst gave the refiner the expected performance while enabling substantial cost savings compared with loading fresh catalyst. This unit successfully produced on-specification product for both modes throughout the duration of the cycle with Excel NiMo on par with the previous cycle loaded with fresh alternative NiMo catalyst. The normalised weighed average bed temperature (WABT) for both cycles is shown in **Figure 2**.

Conclusions

Excel rejuvenated catalysts demonstrated similar activity and stability performance with respect to fresh catalyst for ULSD commercial applications. A substantial cost saving is achieved by the use of rejuvenated catalyst compared to loading fresh catalyst. In one of the catalyst types, the Excel rejuvenated catalyst's HDS activity was higher than a fresh commercial ULSD catalyst. A high throughput reactor unit offers an effective tool for a refiner to ensure that catalyst will provide the best performance for meeting unit objectives prior to buying it.

References

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