EFFECT OF DEACTIVATION METHOD ON THE TESTING PERFORMANCE OF FCC CATALYSTS

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OUTLINE

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- Objectives of the study
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INTRODUCTION

- Laboratory methods for a-priori ranking of FCC catalysts are of major importance for refining industry

- Correct deactivations methods are of equal importance to evaluation methods especially in high metal cases:
  - Metal poisons deposit from crude oil on the zeolite and matrix surface areas
  - Ni is known to act as a dehydrogenation catalyst producing additional hydrogen and coke. It is four times more active than V

- Different types of Lab-Deactivation methods have been proposed in literature

- It is important to best match the Ecat performance (Ecat H2 and coke) in the lab by applying the most suitable deactivation protocol
CPERI: A state of the art FCC Catalyst Evaluation Lab

- Bench and pilot scale FCC independent testing facilities located in Thessaloniki, Greece
- Advanced FCC catalyst characterization techniques
- Fully equipped analytical laboratory
- ISO 9000 and ISO 17025 procedures
- Deactivation and evaluation methods to mimic FCC units
- Research activities on fossil fuels (and bio-fuels) for development of FCC catalysts/additives evaluation technology
- CPERI has collaborated with more than 80 refineries worldwide for different studies in the FCC catalyst testing area
FCC Catalyst Deactivation Units in CPERI

- All FCC deactivation technologies and protocols are available
  - Steamer: hydrothermal deactivation
  - CPS: metal Mitchell impregnation and ReDOx cycles
  - CDU: metals deposition with feed

- Deactivation units: fluid beds available in bench scale (150-200 gr of catalyst) and large scale (5-6 kg of catalyst)

- Flexibility for changing operating parameters for matching Ecat properties: T, time, number of ReDOx cycles, steam%
FCC Catalyst Evaluation Units in CPERI

- **ACE R+ bench-scale unit**
  - Fixed fluid bed reactor (till 12 gr cat)
  - C/O by varying catalyst mass or run time

- **SCT-MAT bench-scale unit**
  - Fixed bed reactor (till 6 gr cat)
  - C/O by varying catalyst mass

- **SCT-RT bench-scale unit**
  - Fluid bed reactor (till 24 gr cat)
  - C/O by varying catalyst mass

- **FCC pilot plant scale unit**
  - Fully circulating pilot unit with continuous catalyst regeneration (4 kg catalyst)
  - Riser height: 9 meters
OBJECTIVES OF THIS STUDY

- To perform a comparative study between different deactivation protocols applied for catalysts deactivation in the presence of metals
  - CPS vs CDU Deactivation Study
  - Effect of Deactivation Protocol on activity, H2 and coke yields
- To investigate the effect of the amount of Ni (expressed as % of the Ecat Ni) that should be deposited on the fresh catalysts on H2 and coke yields
- To suggest optimum metal target for Ni

It is important to use the appropriate lab-deactivation protocol in order to best match the Ecat properties, activity and especially H2 and coke selectivity
EXPERIMENTAL UNITS OF THIS STUDY
ADVANCED CYCLIC PROPYLENE STEAMING (CPS-3) UNIT

Unit modules:
- **Feed module**: Gases
- **Reactor**: fixed fluidized bed

- **Step-1.** Calcination of the FCAT
- **Step-2.** Metals wet impregnation
- **Step-3.** Calcination of the metallated samples
- **Step-4.** CPS aging with 30 ReDOx cycles at 804°C
  - reduction 50 % (nitrogen+5%C3=) +50 % steam
  - stripping 50 % nitrogen +50 % steam
  - oxidation 50 % (4000ppm SO2 in air) + 50 % steam
  - stripping 50 % nitrogen + 50 % steam
  
  **The final 30th cycle consists of:**
  - reduction 50 % (nitrogen+5%C3=) +50 % steam

- **Step-5.** Cooling
PILOT SCALE CYCLIC DEACTIVATION UNIT (CDU) AND PROTOCOL APPLIED

Unit modules:
- **Feed module**: VGO and the metals.
- **Reactor**: fixed fluidized bed

No of cycles for metals deposition: 14. Each cycle consists of:

- Pyrolysis step
- Stripping step
- Heat up to with N2
- Regeneration step
- Steaming step
- Cooling step

At the end of CDU we further age the catalysts by applying a number of CPS cycles in a certain temperature
Circulating Riser Reactor (CRR)

- Catalyst circulation with continuous regeneration
- Solid circulation control by slide valves
- Riser of 9 meters for full simulation of commercial FCC units
Nickel is cracked on surface and mostly remains concentrated in the outer edge of particle.

- V distribution is uniform in both methods and in Ecats.
- In the lab, Ni distribution is best matched with CDU technique.

High metals dehydrogenation activity in CPS-3 samples.

However, metal accuracy and deactivation time are better in CPS-3.
RESULTS AND DISCUSSIONS

TESTING PERFORMANCE DIFFERENCE BETWEEN CDU and CPS METHODS

CASE I
CATALYST FORTRESS TECHNOLOGY
## CATALYST PROPERTIES

<table>
<thead>
<tr>
<th>NAME</th>
<th>Fortress Fresh CPERI</th>
<th>Fortress CPS CPERI</th>
<th>Fortress CDU CPERI</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEACTIVATION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEASURED</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSA, m²/gr</td>
<td>327.60</td>
<td>197.32</td>
<td>191.95</td>
</tr>
<tr>
<td>ZSA, m²/gr</td>
<td>259.41</td>
<td>151.26</td>
<td>145.45</td>
</tr>
<tr>
<td>MSA, m²/gr</td>
<td>68.19</td>
<td>46.07</td>
<td>46.50</td>
</tr>
<tr>
<td>Z/M</td>
<td>3.80</td>
<td>3.28</td>
<td>3.13</td>
</tr>
<tr>
<td>UCS, Å</td>
<td>24.59</td>
<td>24.30</td>
<td>24.32</td>
</tr>
<tr>
<td>Ni, ppmw</td>
<td>0</td>
<td>4940</td>
<td>4325</td>
</tr>
<tr>
<td>V, ppmw</td>
<td>0</td>
<td>1070</td>
<td>1140</td>
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</table>
CASE I – FORTRESS TECHNOLOGY (CPS vs CDU)

- Type of deactivation affects significantly the performance of Fortress technology
- CDU technology is the best deactivation technology for this catalyst at this high Ni levels giving much less coke and H2 yield
Gasoline selectivity and activity are better for the CDU sample.
Despite the high coke from the CPS sample the LCO is not affected by deactivation technology.
CASE II

Effect of Deactivation Protocol on the Performance of High Z/M and Low Z/M FCC Catalysts
A low Z/M (L-Z/M) (<1.0) and a high Z/M (H-Z/M) catalyst were deactivated both by CPS and CDU protocols.

The metal levels on the Dcats were 50% of the Ecat metals.

All 4 Dcats and the 2 Ecats were tested in the pilot plant with the same feed.

<table>
<thead>
<tr>
<th>NAME</th>
<th>L-Z/M Fresh</th>
<th>L-Z/M CPS</th>
<th>L-Z/M CDU</th>
<th>L-Z/M Ecat</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEACTIVATION</td>
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<td></td>
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<tr>
<td>Z/M</td>
<td>0.93</td>
<td>0.63</td>
<td>0.66</td>
<td>0.96</td>
</tr>
<tr>
<td>Ni, ppmw</td>
<td>0</td>
<td>3000</td>
<td>3000</td>
<td>6000</td>
</tr>
<tr>
<td>V, ppmw</td>
<td>0</td>
<td>600</td>
<td>600</td>
<td>1200</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NAME</th>
<th>H-Z/M Fresh</th>
<th>H-Z/M CPS</th>
<th>H-Z/M CDU</th>
<th>H-Z/M Ecat</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEACTIVATION</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z/M</td>
<td>2.3</td>
<td>2.3</td>
<td>2.4</td>
<td>2.6</td>
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<tr>
<td>Ni, ppmw</td>
<td>0</td>
<td>3000</td>
<td>3000</td>
<td>5995</td>
</tr>
<tr>
<td>V, ppmw</td>
<td>0</td>
<td>660</td>
<td>660</td>
<td>1300</td>
</tr>
</tbody>
</table>
CASE II – CPS vs CDU

- The Ecat testing gives lower coke of both Dcats at the same conversion.
- The differences between the coke yields are quite important and the applied deactivation protocol seems to play a significant role.
- In the CPS Dcats the coke difference is 0.8 %wt while in the CDU Dcats it is 0.35%wt.
- CDU simulates much better than CPS the coke selectivities (both in absolute values and deltas).
CASE II – CPS vs CDU/CPS

- Despite the 50% metals on the Dcats the Ecat testing gives slightly lower H2 of both Dcats at the same conversion.
- In the CPS Dcats the H2 difference is 0.12 %wt while in the CDU Dcats it is 0.08 %wt.
- CDU simulates better than CPS the H2 yields.
CASE II – CPS vs CDU/CPS

- Type of deactivation has no effect on LCO
- Both protocols present L-Z/M catalyst as the best for LCO production
OPTIMUM METAL TARGET FOR Ni DEPOSITION ON CPS

- Metal ladder studies are necessary for determination of Ni (and V) levels on Dcat for optimum simulation of Ecat.
- The optimum Ni level depends on the Ni level of the Ecat itself.
- For an Ecat with a high Ni, we should deposit ~50-60% of the Ecat Ni in order to achieve a H2 Dcat/H2 Ecat ratio (and coke as well) close to 1.
Each point is a refinery case

By depositing Ni on the Dcat in the range of 45-70% of the Ecat Ni leads to a H2 Dcat/H2 Ecat yield ratio from 0.8 – 1.2 (i.e. close to 1)

The exact Dcat Ni value depends on Ni level and on the matrix SA
  - The higher the Ni on Ecat or the highest the MSA, lower Ni values on Dcats are needed
This can be done through a process model

For this purpose CPERI spin-off company “PETROCAT” offers integrated catalyst evaluation services to refineries

Through the available in Petrocat FCCTEk model (tuned to our pilot plant operation) we estimate catalyst factors from the pilot plant tests of all candidate catalysts

These coke catalyst factors are applied to the catalytic coke and strippable coke and not to the additive (feed) and metals coke

Thus, an absolute difference in coke yield (between a High MSA and a Low MSA catalyst) of 0.3%wt in the pilot plant can be 0.2%wt in the commercial unit (depending on the contribution of metals and additive coke in the total coke yield)
CONCLUSIONS

- Proper catalyst deactivation methods are necessary for correct catalyst evaluations studies.
- Applied deactivation technology is refinery specific and can be determined only after appropriate deactivation studies.
- For high Ni cases (>2000 ppmw) and low Z/M catalysts the CDU technology is better than CPS-3.
- For both CDU and CPS-3 only a fraction of Ecat metals should be deposited on the catalysts before testing.
- Proper catalyst deactivation combined with FCC pilot plants (Riser) evaluation correctly predicts absolute yields of feeds and catalysts.
- Catalyst testing on pilot scale is very important in terms of refinery reliability and profitability.
  - Prevents operation/economical upsets by in unit trials.
  - Improves economics by selecting best catalyst technology.
- Pilot scale catalyst selection combined with an FCC process model offers significant optimization benefits to refineries.
  - Through the CPERI spin-off company “PETROCAT” we offer such integrated services to refineries.