Nilanjan Brahma

EURECAT USA

Nilanjan has close to 20 years of experience in development and technical support involving hydroprocessing catalysts and catalyst sulfiding and preactivation. Nilanjan is currently the Business Manager for EURECAT’s global Nickel Sulfur Guard services that are utilized in trace sulfur removal from reformer and ISOM feeds. In addition to this there remains a strong involvement with R&D.

Prior to joining Eurecat France in 1992, Nilanjan worked in the hydroprocessing catalyst development group at AkzoNobel (now ALBEMARLE) in Amsterdam (NL). He holds a PhD from the University of Utrecht (The Netherlands) in heterogeneous catalysis and is co-author of numerous articles and patents in the field of catalyst regeneration and preconditioning.

EURECAT USA Inc.
1331 Gemini Street Suite 310
Houston TX 77058, U.S.A.
Phone: +1 832 284 0609
Fax: +1 281 218 9850
Website: www.eurecat.com
E-Mail: nbrahma@eurecat.com
ABSTRACT

CATALYST PREADIVATION USING EURECAT TOTSUCAT® CFP TECHNOLOGY

Randy Alexander, Jim Robinson, and Nilanjan Brahma
EURECAT US Inc. Houston TX

Activation of catalysts in commercial hydroprocessing units is typically done by injecting a sulfur containing compound such as DMDS, DMS, DMSO, or TBPS54 during the startup phase, or in some cases using sour gas or using the sulfur present in the feedstock. When sulfur containing chemicals are concerned, this will require a setup for injecting these into the reactor system and may raise potential HSE issues related to handling these hazardous chemicals. After the activation phase is complete, the catalyst is typically allowed to stabilize for 3-5 days on virgin feed prior to the introduction of cracked feed stocks. Introducing cracked stocks too early can cause irreversible catalyst activity loss due to excessive coke and gum formation.

EURECAT has developed a patented technology that allows the start up of a hydrotreating unit WITHOUT the introduction of the sulfur containing chemicals mentioned above. This ex-situ process, called TOTSUCAT®, ensures complete activation and sulfiding of the catalyst prior to loading in the reactor.

When TOTSUCAT is applied, the following benefits are generally observed:

- The formation of sour water is eliminated; as a rule of thumb, the quantity of sour water formed during startup with in-situ sulfiding is roughly equivalent to 10wt% of the catalyst as loaded.

- Potential exotherms are prevented: the highly exothermic sulfiding reactions have already taken place ex- situ prior to loading.

- Minimal H₂S partial pressure: in the initial phase of a TOTSUCAT startup, an equilibrium will be established when hydrogen is passed over the catalyst bed. In recycle mode, this quantity of H₂S will never exceed a few hundred ppms. This protects sulfur-sensitive catalysts downstream such as reformer and isomerization catalyst. In addition, there is not a need to sample the gas stream during startup, eliminating a potential H₂S exposure hazard for the operators.

- No additional hydrogen is needed: since the catalyst is preactivated and sulfided, no additional hydrogen will be needed to complete the sulfiding process. This lightens the duty on the hydrogen make-up compressor in the s/u phase. As a rule of thumb a quantity of hydrogen comparable to about 1wt% of the catalyst weight is consumed during in-situ sulfiding, or about 2scf/lb of catalyst.
TOTSUCAT is often applied in cases where the unit has temperature limitations that prevent a complete and thorough activation of the catalyst.

TOTSUCAT CFP is an enhanced treatment that combines the benefits of preactivation with the ability to start up a unit with cracked stocks. TOTSUCAT CFP eliminates the requirement to delay the introduction of cracked feeds for 3-5 days after startup. The CFP treatment reduces the acidity of the catalyst, making it suitable for the early introduction of cracked stocks. This may be essential when considering the potential use of TOTSUCAT on catalysts applied in the Resid hydrocracking application field.

TOTSUCAT CFP has been commercially applied in numerous North American refineries.
Catalyst Preactivation
Using EURECAT TOTSUCAT Technology

Nilanjan Brahma
EURECAT US Inc.
Sulfiding of Hydrotreating Catalysts

Oxide catalyst
Polymolybdate structure
Mo$_7$O$_{24}^{6-}$

Sulfided catalyst
Lamellar structure
MoS$_2$ slabs

Temperature
H$_2$ + Sulfiding Agent
CoMo Catalyst
Active Phase Structure

«CoMoS»

S
Mo
Co

0.615 nm
(0002)

Alumina

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NiMo Catalyst Active Phase Structure

Morphology of an activated Ni-Mo-S / Au Structure (STM Picture)

Courtesy of (Haldor Topsoe)
STM Images of Co-Mo-S / Au

Co-Mo-S Nanocrystal  MoS$_2$  MoS$_2$ + Co

Courtesy of (Haldor Topsoe)

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Sulfur Vacancies

When exposed to H₂ atoms, MoS₂ forms two S vacancies

Courtesy of (Haldor Topsoe)
Sulfiding of Hydroprocessing Catalysts

Chemical Reactions
(for every sulfiding agent and method)

\[
\begin{align*}
\text{MoO}_3 + 2 \text{H}_2\text{S} + \text{H}_2 & \rightarrow \text{MoS}_2 + 3 \text{H}_2\text{O} \\
\text{WO}_3 + 2 \text{H}_2\text{S} + \text{H}_2 & \rightarrow \text{WS}_2 + 3 \text{H}_2\text{O} \\
9 \text{CoO} + 8 \text{H}_2\text{S} + \text{H}_2 & \rightarrow \text{Co}_9\text{S}_8 + 9 \text{H}_2\text{O} \\
3 \text{NiO} + 2 \text{H}_2\text{S} + \text{H}_2 & \rightarrow \text{Ni}_3\text{S}_2 + 3 \text{H}_2\text{O}
\end{align*}
\]

Sour Water Produced: Approximately 10 wt\% of catalyst weight
Hydrogen Consumption: Approximately 1 wt\% of catalyst weight
What is Totsucat®?

Totsucat = **Totally Sulfided Catalyst**

The catalyst is preactivated, not just “presulfided”.
Totsucat Processes

- Proprietary patented processes
- All available active metal sites are sulfided
- Homogeneous sulfiding
- Customized solutions available
Typical Totsucat Applications

- Any Critical Path Unit – the cost of unit downtime typically outweighs the cost of Totsucat preactivation by a significant margin
- Any Unit that cannot achieve adequate temperatures required for sulfiding – insufficiently sulfided catalysts cannot perform as designed
- Any Unit upstream of an H₂S sensitive unit such as a Reformer or Isom Unit
- Any Unit that can benefit from starting up with Cracked Feeds
Totsucat Benefits

- Load-and-Go reactor startups
- No exotherms
- Minimal sour water formation
- No additional $H_2$ needed at startup
- Negligible amounts of $H_2S$ released
- No odors
- No handling of sulfiding chemicals
- Catalyst performance is maximized
- Upset conditions will not damage the catalyst
Startup with In-Situ Sulfiding
Liquid phase with SR Feed

- **DMDS**
- **Cracked feed**

**Temperature (°F)**

- **200**
- **390**
- **575**
- **750**

- **SR Feed**
- **Drying step**
- **H₂S breakthrough**
- **Stop DMDS**
- **Secondary Sulfiding**

- SR Feed + DMDS at 175-300°F
- Monitor H₂S at outlet
- Sulfide at 600-660°F
- Sulfiding 3 days of SR feed
- completed in 15-24 hrs

**Timeline:**
- **6 hours**
- **12 hours**
- **18 hours**
- **3 days**

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Totsucat G Startup
Liquid phase with SR Feed

Temperature (°F)

Straight Run feed

SR Feed introduction at low T (175-300°F)
Go to Start of Run Temp in only 6-10 hours
SR Feed for 3-4 Days
Progressively switch to cracked feed
Advantages: Simple startup procedure.
No risk of event which could damage the catalyst

Cracked feed

6 12 18 hours 3 days

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Totsucat G Applications

- Primarily for Type I Catalysts used in Light End Applications – Naphtha, Gasoline Post-treat, Pygas, Tail Gas, H₂ Plant
- Applied commercially to:
  - Albemarle – KF-841, KF-647
  - ART - AT-724G, AT-535, HOP-473K
  - Axens - HR-426, HR-845, HR-806, TG-107
  - Criterion - DN-200, DN-3310, C-424
  - Haldor Topsoe - TK-527, TK-431, TK-437
- Normally supplied as non-passivated
- Also used in:
  - Petrochem Units
  - Lube Units
Totsucat D Applications

- Distillate Hydrotreaters - ULSD
- For some of the latest generation Type II catalysts
  - STARS KF-757
  - ART CDXi
  - Topsoe BRIM
- Process being evaluated for some other catalyst types
Totsucat HC/Totsucat N Applications

- For Hydrocracking and Hydrocracker Pretreat Catalysts
- Totsucat HC for Hydrocracking catalysts
  - Successfully tested on HC-26 by UOP
- Totsucat N for Type II Hydrocracker Pre-treat (HCPT) catalysts
  - Albemarle KF-848 STARS
  - ART NDXi
Totsucat E (formerly Sulficat® E)

- Majority of active metal sites are sulfided
- Sulfur in the feed completes the sulfiding process during a four hour finishing step at startup.
- For units with Sufficient Sulfur in the Feed (S > 0.5%) and capable of reaching >600°F (315°C)
- Passivation is available for loading under air
Totsucat E Applications

- FCC Feed Hydrotreaters, Diesel Units, VGO Units, Resid Units
- Applied commercially to:
  - Criterion - DN-3551, DC-2551, MaxTrap, RN-412, C-411, and DN-200
  - ART – AT-575, HOP-492K, HOP-608
  - Albemarle – KF-841, KF-901, KF-647
  - Haldor Topsoe – TK-551, TK-525, TK-559
  - Axens – HR-538, HR-438
Totsucat E for Fixed Bed VGO Units

- Totsucat E was successfully used to preactivate 1.6 million pounds (725 MT) for 2 different VGO Units
- In-situ sulfiding of these units would have required 48-72 hours and produced approximately 20,000 gallons (75,000 liters) of sour water.
- With preactivation, the unit was online in 12 hours with less than 50 gallons (190 liters) of water removed from the separator.
For Totsucat E - Introduce feed at 80°C; at least 75% of normal rate; recycle back to feed line;

WETTING PHASE

GAS PHASE DRYING STEP 4h @ 150°C

INITIAL SULFIDING 12h @ 220°C

SECOND STAGE SULFIDING 6h @ 320°C

For DMDS - Introduce feed at 120°C;

WETTING PHASE

SECOND STAGE SULFIDING 6h @ 320°C

H2S BREAK THROUGH

Totsucat E vs DMDS Startup Time

Time Gain
TOTSUCAT E vs DMDS: 48 hrs

Activation Complete

Gas Phase Heat up Rate @ 4°C/hr

Liquid Heat Up rate @ 17°C/hr S content S >> 0.5 wt%
Totsucat Properties

- Sulfides are sensitive to oxidation by air
- Product is classified in all cases as:
  - **Self-heating Solid** (Class 4.2, UN 3190, Packaging Group II or III)
- Two types of formulations depending on the application type or customer preference:
  - Oil Passivation – Allows for loading under air
  - Non-passivated – Requires inert loading
- Treated catalyst is packaged in bins or metal drums with metalized liners
Issue of Cracked Feed

Cracked Feeds contain olefins, di-olefins, and other polynuclear aromatics (PNA) that form gums and tars when exposed to hyper-active sites on freshly sulfided catalysts.
Issue of Cracked Feed

Gums and tars formed during startup are readily deposited on the catalyst surface.

These deposits will block the catalyst pores and active sites, leading to a permanent loss of catalyst activity.
Issue of Cracked Feed

To avoid this problem, catalyst manufacturers recommend a break-in period of at least three days using only straight run feed at startup.

By running only straight run feed, a small amount of coke will form on the catalyst surface, gradually reducing the hyperactivity of the catalyst.
Issue of Cracked Feed

Delaying the introduction of cracked feeds can have significant costs:

- Lost profits from processing cracked and heavy feeds.
- May need to purchase additional straight run feed for startup.
- Storage costs for a sufficient quantity of straight run feed required at startup.
- Storage costs for cracked feeds that must be held for processing later.

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Solution: Totsucat CFP

- CFP = Cracked Feed Protection
- In addition to Totsucat preactivation, Totsucat CFP has carbon carefully deposited on the catalyst surface which moderates the hyper-active sites.
- Catalytic acidity is also reduced.
Totsucat CFP Benefits

- Totsucat CFP allows direct introduction of cracked feeds at 175-450°F
- Provides normal cycle lengths without waiting 3-4 days before adding cracked feeds
- No additional SR required
- No storage of cracked feeds during startup
Case Study – NHT with Totsucat CFP

Naphtha Hydrotreater

Feed: 20% Coker Naphtha/80% Straight Run

Feed Rate: 35,000 BPD

Catalyst Type: NiMo

Catalyst Quantity: 53,000 pounds
Case Study – NHT with Totsucat CFP

- **Run 1** – In-situ Sulfiding with 3 Day Break In – Catalyst A, Sock loaded
- **Run 2** – Totsucat CFP Preactivation – Startup with 20% cracked feed – Catalyst A, Dense loaded
- **Run 3** – Totsucat CFP Preactivation – Startup with 20% cracked feed – Catalyst B, Sock loaded

Note - Unit is heat limited due to fouling.
Case Study – NHT with Totsucat CFP

Reactor Temperature

- WABT - In-situ with Break In
- WABT - Totsucat CFP Run 1
- WABT - Totsucat CFP Run 2

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Case Study – NHT with Totsucat CFP

ΔT – Inlet to Bottom

- Inlet to Bottom ΔT - In-Situ with Break In
- Inlet to Bottom ΔT - Totsucat CFP Run 1
- Inlet to Bottom ΔT - Totsucat CFP Run 2

Days on Oil

Temperature (°F)

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Case Study – NHT with Totsucat CFP

Coker Naphtha Feed Rate

- Coker Naphtha - In-situ with Break In
- Coker Naphtha - Totsucat CFP Run 1
- Coker Naphtha - Totsucat CFP Run 2

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Startup with Totsucat CFP
Liquid Phase with Cracked Feed

Introduce cracked feed at 175-450°F
Heat up at 35°F/h up to 475°F
After 475°F Heat up at 20°F/h up to SOR.

Advantages: Safe fast start-up; Additional 3 to 4 days of cracked feed processed; No need for SR or Cracked Feed storage
Totsucat Processing Sites

USA – Pasadena, Texas

Europe – Gela, Italy

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Totsucat Commercial Experience

Over 300 Totsucat Projects Completed at EUS totaling 16+ million pounds of catalyst (June 2009)

- **FCC Naphtha HDS**
  Various hydrotreating catalysts
- **VGO HDS Unit**
  Unit with over 1.6 million pounds of catalyst started up in 12 hrs
- **Selective Hydrogenation (chemical application)**
  NiMo catalysts
- **Selective Hydrogenation of Pyrolysis Gasoline**
  CoMo catalysts
- **Coker Naphtha Hydrotreater**
  Totsucat CFP on NiMo catalyst – on fifth cycle with Totsucat CFP
- **Wax Hydrofinishing**
  NiW catalysts
- **Tail Gas Units** – Totsucat provides the easiest method for starting a Tail Gas Unit
Eurecat Contact Information

- **Randy Alexander – Business Manager for Sulfiding Technologies**
  - Email: Randy.Alexander@eurecat.com
  - Office: 832.284.0612
  - Cell: 832.659.7302

- **Dr. Nilanjan “Babu” Brahma – Business Manager**
  - Email: Nilanjan.Brahma@eurecat.com
  - Office: 832.284.0609
  - Cell: 832.659.7301

- **Chris Buffington – International Sales Manager**
  - Email: Chris.Buffington@eurecat.com
  - Office: 832.284.0608
  - Cell: 281.703.0575

- **Tony Loverdi – Resale Catalyst Manager**
  - Email: Tony.Loverdi@eurecat.com
  - Office: 832.284.0607
  - Cell: 281.380.8121

- **Jim Robinson – Business Manager for Olefins and Petrochem**
  - Email: Jim.Robinson@eurecat.com
  - Office: 832.284.0602
  - Cell: 281.635.6100
• Totsucat CFP – Cracked Feed Protection
A period of 2-3 days is usually recommended before cracked stocks introduction. This is for letting the catalyst gently coke at SOR conditions with an olefin/di-olefin free feed.

A specific Totsucat product can address this problem: **Totsucat CFP** (Cracked Feed Protection). It contains already some carbon deposited on catalyst surface.

Then cracked feed may be directly introduced at low temperature, with a slow heat-up phase to SOR temperature (Direct introduction of cracked feed at SOR temperature is not recommended).
TOTSUCAT CFP : START-UP GUIDELINES

TOTSUCAT CFP START-UP: cracked feed intro at low T

- Temperature (°C)

- Cracked feed

- Direct cracked feed introduction at 80-120°C,
  - Heat up at 20°C/h up to 250°C,
  - Heat up at 10°C/h up to SOR.

- Advantages: safe start-up, very quick (3 to 4 days are saved), no need of SR feed storage
Evidence that Totsucat CFP protects the catalyst

Coke and gums formation is related to the interaction between acidic sites and unsaturated molecules.

How to prove that Totsucat CFP decreases acidity?
Use of a ortho-xylene Isomerization test

The more acidic the catalyst, the higher the Isomerization rate
Validation of the o-xylene isomerization testing for characterizing acidity

Increase of the isomerization rate – in line with increase of the acidity of the catalyst

NiMo Totsucat G Low acidity alumina
CoMo1 Totsucat G Standard alumina Medium acidity
CoMo2 Totsucat G Standard alumina High acidity

O-xylene isomerization test is sensitive to the acidity of different known catalysts

Eurecat – Totsucat CFP
Evidence that Totsucat CFP protects the catalyst

- CoMo1 Totsucat G
  - Standard alumina
  - Medium acidity
- CoMo1 Totsucat CFP
  - Standard alumina
  - Medium acidity
- CoMo2 Totsucat G
  - Standard alumina
  - High acidity
- CoMo2 Totsucat CFP
  - Standard alumina
  - High acidity

CFP treatment lowers the acidity of the catalyst → less coke and gum formation

Eurecat – Totsucat CFP