Meeting the Challenges of ULSD

Understanding the Chemistry and Kinetics

- Catalyst Chemistry – Designing for ULSD
  - Type I Catalysts
  - Type II Catalyst & Use of Chelates
- HDS & HDN/HDA Reaction Pathways
  - The right catalyst for the desired reaction
- Optimizing the Catalyst System
  - Factors Influencing Optimum Configuration
  - Activity vs. Hydrogen Consumption
- Exploiting PNA Hydrogenation Kinetics
  - Improving Hydrogenation Selectivity
  - Use of ART’s SRO Technology

Summary
Catalyst Surface Chemistry – Type I Catalyst Activity

- Co & Ni in solution interact with the alumina support or Mo species
- Mo sulfides at a higher temperature than Co or Ni
  - MoS$_2$ formed at a higher temperature has a less sulfided, less crystalline structure
  - Has strong interactions with the support
- Sulfidation of Co/Ni relative to Mo occurs first (Evidence from XPS)
- Metals stay are not as highly dispersed through the sulfiding step as possible
  - Increases concentration of Type I sites
  - Increases concentrated areas of metals on alumina surface
Type I Sites

- Fewer NiS at edges
- Ni interactions with alumina
- Mo interactions with alumina
- Mo not fully sulfided, Less MoS$_2$ stacking
Catalyst Surface Chemistry – Type I Catalyst Activity

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XPS of ‘Standard’ CoMo Catalyst

Mo Spectra

- Sulfided at 260 F
- Sulfided at 575 F
- Sulfided at 755 F
- Fresh
Creating the “right” Catalyst by use of Chelating Agents

Amino acids
- EDTA
- Ethylene glycol
- Citric acid
- Monoethanol amine
- Diethylene glycol monoethyl ether
- Ethylenediamine
- Triethylenetriamine

Added to a ‘typical’ NiMoP or CoMoP solution and Drying at low temperature

Bidentate: Latin, “two-toothed”
\[ \text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2 \]

Tridentate: Latin, “three-toothed”
\[ \text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{CH}_2\text{-NH}_2 \]
Chelates: Controlling Surface Chemistry

- Chelate Binds preferentially to Co/Ni ions (Evidence UV-Vis)
  - Reduces the activity of Co/Ni in solution so it does not readily interact with the alumina support or Mo species
  - Mo sulfides at a lower temperature
    - MoS$_2$ formed at a lower temperature is more fully sulfided and has a more crystalline structure
    - Has only weak interactions with the support allowing stacking
    - The adsorption of an aromatic ring is enhanced by the regularity of the edges of MoS$_2$ thus aromatic saturation is improved
  - Delays sulfidation of Co/Ni relative to Mo (Evidence from XPS)
  - Once Co/Ni are released by chelate during sulfidation they move to the edges of the MoS$_2$ slabs
  - Metals stay highly dispersed through the sulfiding
    - Increases concentration of Type II sites
Type II Sites

- MoS$_2$ Slabs
- NiS
- Alumina support

- More Rim-Edge sites in two stacks compared to one tall stack
- More NiS at edge sites
- No Ni interactions with alumina
- Mo is more fully sulfided
- Weak Mo-alumina interactions - taller stacks than Type I
XPS of Chelated CoMo Catalyst

Mo Spectra

Mo sulfide appears at 260 °F for chelated catalyst

Sulfided at 755 °F
Sulfided at 575 °F
Sulfided at 260 °F
Fresh

Normalized Intensity

Binding Energy (eV)
Activity Comparison

Conditions: 1.5 LHSV, 800 psig, 1200 SCFB H2/Oil ratio
Feed: SR, 33.7 API, 0.568 w% Sulfur & 221 ppm Nitrogen
Classification of Diesel Sulfur Species

Decreasing Rate Constant

Increasing Boiling Point

“Easy” sulfur

“Hard” sulfur
Reaction Pathways for Diesel HDS

Low Sulfur Diesel

NiMo

Ultra Low Sulfur Diesel

CoMo

\[ \text{NiMo} \quad +H_2 \quad \rightarrow \quad \text{CoMo} \quad -H_2S \quad +H_2 \]

\[ \text{Ultra Low Sulfur Diesel} \quad +H_2 \quad \rightarrow \quad \text{Low Sulfur Diesel} \quad -H_2S \quad +H_2 \]

Advanced Refining Technologies
Poly Aromatics Hydrogenation & How it Occurs

\[ \text{naphthalene} \quad \leftrightarrow \quad \text{tetralin} \quad \leftrightarrow \quad \text{decalin} \]

\[ k_1 \text{ roughly } 10 \times k_2 \text{ for naphthalenes} \]

\[ \text{biphenyl} \quad \leftrightarrow \quad \text{tetralin} \quad \leftrightarrow \quad \text{decalin} \]

\[ k_3 \text{ is roughly } 5 \times k_4 \text{ for biphenyls} \]
Aromatics Concentration Profile

1st order reversible reactions in series

$k_1 = 10 \times k_2$

Graphic showing relative concentrations of 2-ring aromatic, mono aromatic, and saturated components over residence time.
Sulfur minimization by ART

The SmART Catalyst System™

◆ A staged catalyst loading designed to optimize both reaction pathways:
  ▪ A high activity CoMo catalyst (420DX, CDXi) is used to catalyze the direct abstraction route
    ☀ Removes unhindered or “easy” sulfur more efficiently
  ▪ A high activity NiMo catalyst (AT580, NDXi) is used to catalyze the saturation/abstraction route
    ☀ Removes hindered or “hard” sulfur more efficiently

◆ A properly staged loading of two High Activity Catalysts provides better performance
  ☀ Balancing activity and hydrogen consumption
Effects of HDS Operating Severity

1.0 LHSV, 590 Psi H₂, 2000 SCFB H₂/Oil
28.7 API, 1.78 w% sulfur, 370 ppm Nitrogen

CoMo outperforms NiMo
NiMo outperforms CoMo
SmART Catalyst System Has Highest Activity

Cond: 1.0 LHSV, 590 Psig & 2000 SCFB H₂/Oil
Feed: 28.7 API and 1.78 wt% Sulfur
Fraction Hard Sulfur Increases with Endpoint

![Graph showing the relationship between Fraction Hard Sulfur and Feed T90 by D86, °F. The graph includes data points for LCO, LCGO, and SR, with LCO represented by blue triangles, LCGO by red circles, and SR by green diamonds.](Image)

Advanced Refining Technologies
Feedstock Effects on Activity - CoMo Catalyst

NiMo Catalyst shows different response:
- Handles EP better
- Nitrogen effect more severe
Hydrogen Availability

The graph illustrates the relative HDS rate constant as a function of H₂/Oil / H₂ Consumption for different conditions:

- **High Pressure**
  - SR
  - 20% LCO

- **Low Pressure**

The graph shows two lines for each condition, representing the relative HDS rate constant at varying H₂/Oil / H₂ Consumption levels.
Optimizing HDS Activity and H₂ Consumption

Conditions: 1.0 LHSV, 590 Psi H₂ & 2000 SCFB H₂/Oil
Feed: 30% LCO blend with 28.7 API and 1.78 wt% Sulfur
Hydrogen Consumption on LCGO

NiMo hydrogenates more poly and mono aromatics resulting in much higher hydrogen consumption compared to CoMo.
HDS Activity at High Pressure

Feed: 15% LCO blend, 31.46 API and 0.61 wt% Sulfur
Treated at 1000 Psig

Product Sulfur, ppm

1/LHSV, hr

CoMo
NiMo
Aromatics Hydrogenation at High Pressure

15% LCO Blend Treated at 1000 Psig

CoMo Catalyst

NiMo Catalyst

Concentration, %

Relative Time in Reactor

300 SCFB Difference in $H_2$ consumption!

Poly aromatic
Mono aromatic
Saturated
Designing the Best Catalyst System

• Feedstock Properties are Critical
  ▶ “Hard” Sulfur content (feed end point)
  ▶ Nitrogen content
  ▶ Aromatics content

• Hydrogen Availability
  ▶ $H_2$/Oil ratio and $H_2$ Pressure
    ● Hydrogenation Activity and Selectivity are key
    ● Equilibrium constraints must be considered

• These all determine the optimum SmART System
Cetane Index of Various Distillate Feed Sources

![Graph showing the cetane index of various distillate feed sources. The x-axis represents the feed API, and the y-axis represents the cetane index (D976). The graph includes data points for LCO, LCGO, SR, and KEROSENE, each represented by different markers.](image-url)
Refiner’s Ability to Increase Product Cetane

Cetane Index Increase

Feed API Gravity

100% LCO → No LCO
Cetane number improvement in Diesel feeds

- Poly Aromatic Naphthalenes
  - Δ Cetane number: 10-15

- Mono Aromatic
  - Δ Cetane number: 10-15

- Tetralins
  - Δ Cetane number: 15-45

- Saturate
  - Δ Cetane number: 12-15

- Decalins
  - Δ Cetane number: 25-65

- n-Decane
  - C_{10}H_{22}
  - Δ Cetane number: 60-70

- n-Paraffins
  - Δ Cetane number: 60-70

- Iso-Paraffins
  - Δ Cetane number: 25-65
Impact of Catalyst System on Cetane Increase

![Bar chart showing the impact of NDXi and NDXi/SRO on cetane index improvement.](chart.png)
Hydrogen Consumption for Cetane Index Improvement

H₂ Consumption / Unit Cetane Improvement, SCFB

- NDXi
- NDXi / SRO
SmART Catalyst System

- CoMo catalyst alone may not have sufficient hydrogenation activity to achieve < 10 ppm sulfur

- NiMo catalyst alone is very efficient at catalyzing aromatic saturation reactions
  - Sometimes too good resulting in saturation of Mono-aromatics and significantly higher H₂ consumption

- A staged catalyst loading designed to optimize both reaction pathways
  - Provides better performance than use of either CoMo or NiMo
    - Higher HDS activity
    - Minimum hydrogen consumption
  - Utilizes specially designed high activity catalysts ART 420DX, CDXi, and NDXi
SmART Catalyst System: Summary

- Use of Selective Ring Opening catalyst:
  - Lower hydrogen consumption per unit of cetane improvement over conventional systems
  - Lower product Aromatics & PNA’s
  - Increased LCO processing or longer cycle time

SmART Catalyst System™ is a customized loading which ensures operating objectives are met within unit constraints