Modern approaches to designing highly effective hydrotreating catalysts

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Moscow, May 16, 2016
**Introduction.** Hydrotreating processes in oil refinery

**Crude Oil after Desalting**

- **Atm Dist**
  - 180-360 °C
  - IBP-180 °C
  - SRGO

- **Vac Dist**
  - 360-500 °C
  - VGO

- **Coking**
  - > 500 °C

**Deep hydrotreating**

- Gasoline fractions
- Diesel fuel

**Selective hydrotreating**

- FCC

**Target tasks**

- **Gasoline**
  - Remove sulfur to below 0.5 ppm (reforming feedstock)
  - 10-40 ppm (FCC gasoline)

- **SRGO**
  - Remove sulfur to below 50-10 ppm
  - Condensed aromatics hydrogenation

- **VGO**
  - Remove sulfur to below 350-500 ppm
  - Metals removal

**Undesirable reactions**

- Aromatics & olefin hydrogenation
- Cracking
- Cracking
Introduction.
Hydrotreating processes in oil refinery

Challenges in oil refining:
- Worsening of oil crudes
- Stricter environmental requirements to products
- Involvement of bio-raw materials
- Involvement of oil-slime to refining

Crude Oil after Desalting

Atm Dist

SRGO

Vac Dist

VGO

FCC

Selective hydrotreating

Coking

Deep hydrotreating

Deep hydrotreating

Deep hydrotreating

Gasoline fractions

Gasoline

Diesel fuel

IBP-180 °C

180-360 °C

360-500 °C

> 500 °C

180-360 °C

100-220 °C

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Improving catalysts
Introduction. Industrial hydrotreating catalysts

> 100 brands of catalysts
NiMo/Al₂O₃; CoMo/Al₂O₃
NiW/Al₂O₃; NiW/ASA

Particle length 25-60 Å

S = 1.8 % wt. (18 000 ppm)
S = 0.001 % wt. (10 ppm)

H₂ Feedstock

Catalysts 30–100 m³

Product

H₂S

P = 2-10 MPa,
T = 280-420 ºC
Main developed concepts of catalysis by sulfides

"Co(Ni)MoS" phase model


The electronic model of promoting

- S. Harris, R.R. Chianelli // J. Catal. 98 (1986) 17

The "Rim-edge" model

Scientific challenges in sulfide catalysis

Turnover frequency \([\text{mol DBT} \times \text{mol act. site}^{-1} \times \text{s}^{-1}]\)
Scientific challenges in sulfide catalysis

Turnover frequency [mol DBT × mol act. site⁻¹ × s⁻¹]

\[ \text{TOF}_\text{XMS, P, T} = \mathcal{A}(L, N, X, M, n_i, \ldots?) \]

Fundamental questions:

- Intrinsic nature of active sites (electronic, structural)
- “Structure – activity” relationships
- Evolution of active sites at reaction conditions (T, p(H₂), H₂S, N-,O-containing compounds...)
- Support effects (electronic, new compositions, Brønsted/Lewis...)
- Create new active sites (CoMoS-III, NiCoMoS, NiMoWS, ...)
Haldor Topsøe’s grants for PhD students of Samara State Technical University

Alexander Mozhaev  
2011 winner  
**Deep HDS, HYD.**  
Co$_2$Mo$_{10}$HPA based catalysts. NiCoMoS catalysts

Aleksey Pimerzin  
2013 winner  
**Deep HDS, HYD, HDN.**  
Spillover effects in sulfide catalysis

Pavel Nikulshin  
2008 winner  
**Deep HDS of diesel**  
XMo$_6$HPAs as precursors for HDS catalysts. C-coated supports

Daria Ishutenko  
2012 winner  
**Selective HDS of FCC gasoline.**  
KCoMoS catalysts based on PMo$_{12}$HPA

Maria Kulikova  
2015 winner  
**Deep HDS&HYD**  
NiMoWS catalysts based on SiMo$_n$W$_{12-n}$HPA

Aleksey Pimerzin  
2013 winner  
**Deep HDS, HYD, HDN.**  
Spillover effects in sulfide catalysis

Andrey Varakin  
2014 winner  
**HDO reactions.**  
Co-hydrotreating. Unsupported catalysts

**TOF**$_{XMS} = \text{f}(L,N,X,M, \text{n}_i,\ldots?)$
Topics

1. Development of new sulfide catalysts
   1.1 New molecular precursors of active phases
   1.2 Effect of composition and morphology of active phase species on catalytic properties

2. Catalysts for deep hydrotreating of oil fractions
   2.1 Trimetallic NiCoMoS catalysts with enhanced HDS & HYD activities
   2.2 NiW/Al₂O₃ catalysts prepared with heteropolycompounds

3. Catalysts for selective hydrodesulfurization of FCC gasolines
   3.1 Trimetallic KCoMoS catalysts with improved HDS/HYDO selectivity

4. Catalysts for co-hydrotreating of diesel and vegetable oil
   4.1 Carbon-covered supports for sulfide catalysts
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Some problems in preparation of Co(Ni)Mo/Al$_2$O$_3$ catalysts

(1) Impregnation with (NH$_4$)$_6$Mo$_7$O$_{24}$ and Ni(NO$_3$)$_2$

(2) Drying and calcination

(3) Sulfidation

H$_2$S/H$_2$

Drawbacks:
- Co atoms introduced in Al$_2$O$_3$
- Co atoms exists in nonactive Co$_9$S$_8$ species
- MoS$_2$ not fully sulfided and strongly bonded with Al$_2$O$_3$
How to improve HDS catalysts?

- Use of new carriers (C, TiO₂, zeolite, …)
- Use of «Doping» elements (Rh, Pt, Ru, P, F)
- Use of chelating agent in the impregnating solution (NTA, EDTA, …)
- Use of unsupported sulfides and nonsulfide catalysts
- Use of HPA in the impregnating solution (Co₂Mo₁₀O₃₄⁶⁻, PMo₁₂O₄₀³⁻)
- Increase of active metals contents
- Modification of the oxidic precursor by organic agents (TEG, TGA, …)
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Typical HPAs structures used for preparation of hydroprocessing catalysts

Preparation of catalysts with heteropolyanions

Solution of HPA

Impregnation of Al₂O₃

Impregnated carrier

Drying at 110 °C 6 h

Catalyst in oxide state

Sulfdation at 400 °C, H₂S/H₂

Sulfided catalyst

Blue octahedra: MoO₆; green octahedra: octahedral heteroatom (Co); pink tetrahedra: central heteroatom in Keggin structure (P, Si).
**Thiophene hydrodesulfurization (HDS)**

\[
\text{S}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10}
\]

**Conditions:**

Pulse microcatalytic reactor

- \( t = 300 - 400^\circ\text{C} \)
- \( P = 0.125 \text{ MPa} \)
- \( V(\text{H}_2) = 20 \text{ cm}^3/\text{min} \)
- \( V_{\text{thiophene}} = 0.2 \mu\text{L} \)
- \( m = 0.25 \text{ mg} \)

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**Figure:**

- **XMo\textsubscript{6}/Al\textsubscript{2}O\textsubscript{3}**
- **Ni\textsubscript{3}-XMo\textsubscript{6}/Al\textsubscript{2}O\textsubscript{3}**
- **Ni\textsubscript{0.5}-Mo/Al\textsubscript{2}O\textsubscript{3} (400 \textdegree\text{C})**

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Selective HDS of FCC gasoline

Target reaction HDS

$$\text{HDS:} \quad \text{S} + 2\text{H}_2 \rightleftharpoons \text{CH}_2=\text{CH}_2 + \text{H}_2$$

Undesirable reaction HYDO

$$\text{HYDO:} \quad \text{CH}_3\text{CH}=\text{CH}_2 + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_3$$

Conditions:
Bench scale flow reactor
Feedstock: $n$-hexene-1 (36 wt.%), thiophene (0.1 wt.% S), $n$-heptane (solvent)

- $t = 220^\circ\text{C}$
- $P = 1.5 \text{ MPa}$
- LHSV = 5.0 h$^{-1}$
- $\text{H}_2$/feedstock = 100 NL/L;
- $m_{\text{cat}} = 0.3 \text{ g}$
Anderson type XMo$_6$HPA
Physical-chemical properties of the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni(Co)MoS phase, at. %</th>
<th>Ni(Co)$S_x$ phase, at. %</th>
<th>Ni(Co)$^{2+}$ phase, at. %</th>
<th>(Co/Mo)$_{slab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo$_6$/Al$_2$O$_3$</td>
<td>67</td>
<td>8</td>
<td>25</td>
<td>0.14</td>
</tr>
<tr>
<td>CoMo$_6$/Al$_2$O$_3$</td>
<td>71</td>
<td>9</td>
<td>20</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The decomposition of the Mo3d and Co2p XPS spectra were performed using approaches proposed by [1] and with the use of CasaXPS Version 2.3.16 software.

2. K. Marchand et al // Oil & Gas Sci. & Tech. 64 (2009), No. 6, 719

Active phase of the catalysts is Co(Ni)MoS phase with deficiency of promoter atoms
Role of HPA is in the formation of “framework” of an active phase, i.e. multilayer MoS$_2$ slabs.
Anderson type $\text{XMo}_6\text{HPA}$

Sabatier’s principle in catalysis by supported TMS

$\Rightarrow$ Heteroatom $X$ promotes optimization of the electron density on the anti-bonding $d$-orbital of Mo in the active mixed sulfide phase and, thereby, facilitates productivities of the active sites.
Heteropolycompounds as precursors of hydrotreating catalysts

Advantages:
- Application of HPCs gives a possibility to introduce Mo and a promoter (modifiers) into a catalyst simultaneously – from one molecule
- CoMoS phase of type II formed from HPCs

Shortcomings:
- There is no HPA structure with higher Co (Ni)/Mo ratio than 5:1
- Use only HPA as a precursor of catalysts leads to formation of active phase with deficiency of CoMo sites
Heteropolycompounds as precursors of hydrotreating catalysts: overcoming of shortcomings

Use of Co salt of HPAs for catalysts preparation

Heteropolycompounds as precursors of hydrotreating catalysts: overcoming of shortcomings

Use of Co salt of HPAs for catalysts preparation

Thiophene conversion (%) vs. Promoter/Mo

- NiMo₆-emuls
- FeMo₆-emuls
- CoMo₆/Al₂O₃
- Co₂Mo₁₀/Al₂O₃
- Co₃-Co₂Mo₁₀/Al₂O₃
- NiMo₆-emuls
- Co₃/2-PMo₁₂O₄₀/Al₂O₃
- Co₇/2-PMo₁₂O₄₀/Al₂O₃
- Co₂Mo₁₀/Al₂O₃
- CoMo/Al₂O₃ (industrial)

References:
Difficulties in deep hydrodesulfurization of oil fractions

Reactivity of various organic sulfur compounds in HDS versus their ring sizes and positions of alkyl substitutions on the ring

<table>
<thead>
<tr>
<th>Sulfur compound</th>
<th>Relative HDS rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiophene</td>
<td>2250</td>
</tr>
<tr>
<td>Benzothiophene</td>
<td>1330</td>
</tr>
<tr>
<td>Dibenzothiophene (DBT)</td>
<td>100</td>
</tr>
<tr>
<td>4-methyldibenzothiophene (4-MDBT)</td>
<td>9</td>
</tr>
<tr>
<td>4,6-dimethyldibenzothiophene (4,6-DMDBT)</td>
<td>7</td>
</tr>
</tbody>
</table>

σ-bonding

π-bonding

Steric hindrance
Heteropolycompounds as precursors of hydrotreating catalysts: overcoming of shortcomings

\[ k_{\text{HDS}} \times 10^5 \text{ (mol.h}^{-1}.\text{g}^{-1}) \]

- DBT HDS
- 4,6-DMDBT HDS

\[ (\text{Co/Mo})_{\text{edge}} \]

P. Nikulshin et al. // J. Catalysis 312 (2014) 152
Heteropolycompounds as precursors of hydrotreating catalysts: overcoming of shortcomings

- Promotion degree of the MoS₂ edges \((\text{Co/Mo})_{\text{edge}}\) became only 0.64
- Co salt of \(\text{Co}_2\text{Mo}_{10}\) HPA does not provide required molecular contact of \(\text{Co}^{2+}\) with HPA on the alumina surface
How to improve HDS catalysts?

Modification of the oxidic precursor by organic agents (TEG, TGA…)

- Use of new carriers (C, TiO₂, zeolite, …)
- Use of «Doping» elements (Rh, Pt, Ru, P, F)
- Use of chelating agent in the impregnating solution (NTA, EDTA...)
- Use of HPA in the impregnating solution (Co₂Mo₁₀O₃₄⁶⁻, PMo₁₂O₄₀³⁻)

- Increase of active metals contents
- Use of unsupported sulfides and nonsulfide catalysts

What results will be obtained if both HPA and chelating agent are used for catalyst preparation?
Topics

1. Development of new sulfide catalysts
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Simultaneous using Co$_2$Mo$_{10}$HPA and different types of chelating agents

Co complex with chelating agent (NTA, EDTA, CA, TA)

Co$_2$Mo$_{10}$HPA (T=40 °C, aqueous sol.)

[Co(Ligand)]-Co$_2$Mo$_{10}$HPA/Al$_2$O$_3$ catalysts

Drying 110 °C (5h)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Presence in impregnating solution</th>
<th>Amount in the Catalysts (wt. %)</th>
<th>Textural characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co$^{2+}$  NH$_4^+$  Chelating agent</td>
<td>Mo    Co    Co/Mo ratio</td>
<td>SSA (m$^2$/g)</td>
</tr>
<tr>
<td>Co$<em>2$Mo$</em>{10}$HPA</td>
<td>−  +  −</td>
<td>10.0  1.2  0.17</td>
<td>183</td>
</tr>
<tr>
<td>Co$_3$-Co$<em>2$Mo$</em>{10}$HPA</td>
<td>+  −  −</td>
<td>9.9   3.1  0.31</td>
<td>170</td>
</tr>
<tr>
<td>[Co(NTA)$_3$]-Co$<em>2$Mo$</em>{10}$HPA</td>
<td>+  +  NTA</td>
<td>10.0  3.2  0.32</td>
<td>168</td>
</tr>
<tr>
<td>[Co(EDTA)$_3$]-Co$<em>2$Mo$</em>{10}$HPA</td>
<td>+  +  EDTA</td>
<td>10.1  3.0  0.30</td>
<td>172</td>
</tr>
<tr>
<td>[Co(CA)$_3$]-Co$<em>2$Mo$</em>{10}$HPA</td>
<td>+  −  Citric acid</td>
<td>10.1  3.0  0.30</td>
<td>170</td>
</tr>
<tr>
<td>[Co(TA)$_3$]-Co$<em>2$Mo$</em>{10}$HPA</td>
<td>+  −  Tartaric acid</td>
<td>10.1  3.0  0.30</td>
<td>170</td>
</tr>
</tbody>
</table>

Co$_2$Mo$_{10}$HPA (T=40 °C, aqueous sol.)

Al$_2$O$_3$

S$_g$ = 240 m$^2$/g, V$_p$ = 0.7 cm$^3$/g, D$_p$ = 12 nm
### Composition of CoMoS species present at the surface of sulfided catalysts (from TEM and XPS)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>((\text{Co/Mo})_{\text{tot}})</th>
<th>((\text{Co/Mo})_{\text{edge}})</th>
<th>Co in CoMoS and multi-slabs CoMoS' (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(<em>2)Mo(</em>{10})/Al(_2)O(_3)</td>
<td>0.2</td>
<td>0.4</td>
<td>0.14</td>
</tr>
<tr>
<td>Co(_3)-Co(<em>2)Mo(</em>{10})/Al(_2)O(_3)</td>
<td>0.5</td>
<td>0.6</td>
<td>0.43</td>
</tr>
<tr>
<td>Co(_3)[NTA]-Co(<em>2)Mo(</em>{10})/Al(_2)O(_3)</td>
<td>0.5</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Co(_3)[EDTA]-Co(<em>2)Mo(</em>{10})/Al(_2)O(_3)</td>
<td>0.5</td>
<td>0.7</td>
<td>0.21</td>
</tr>
<tr>
<td>Co(_3)[CA]-Co(<em>2)Mo(</em>{10})/Al(_2)O(_3)</td>
<td>0.5</td>
<td>1.1</td>
<td>0.72</td>
</tr>
<tr>
<td>Co(_3)[TA]-Co(<em>2)Mo(</em>{10})/Al(_2)O(_3)</td>
<td>0.5</td>
<td>0.8</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Simultaneous using Co\(_2\)Mo\(_{10}\)HPA with Co(Chel) complexes resulted in formation of CoMoS species fully covered with Co promoter atoms.

Differences in morphological properties of sulfide species connects with the features of the formed supported oxidic precursors that was indicated by Raman.

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*P. Nikulshin et al. // J. Catalysis 312 (2014) 152*
Correlation of reaction rate constants with Co content into CoMoS and multi-CoMoS/ species

**Thiophene HDS**

Good correlation between rate constants of HDS and HYD of “light” molecules and CoMoS phase content and bad – for “heavy” molecules

*DBT*

*4,6-DMDBT*

*St. # ≥ 1*
Correlation of reaction rate constants with Co content into CoMoS and multi-CoMoS species

**Thiophene HDS**

![Graph showing correlation between Co content and reaction rate constants for thiophene HDS.]

**Hexene-1 HYD**

![Graph showing correlation between Co content and reaction rate constants for hexene HYD.]

**Hydrodesulfurization of DBT and 4,6-DMDBT**

![Graph showing correlation between Co content and reaction rate constants for hydrodesulfurization of DBT and 4,6-DMDBT.]

Good correlation between rate constants of DBT and 4,6-DMDBT and multi-slab CoMoS phase content.

Correlation of reaction rate constants with Co content into CoMoS and multi-CoMoS species.
Towards control of selectivity factor HDS/HYD in FCC gasoline HDT: composition and size effects

[Co(Lig)]-Co₂Mo₁₀Al₂O₃ catalysts

Comparison of HDS and HYD activities and selectivity factor of CoMo-supported catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activity</th>
<th>SF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoMo/Al₂O₃-1</td>
<td>30.9</td>
<td>58.2</td>
<td>0.42</td>
</tr>
<tr>
<td>CoMo/Al₂O₃-2</td>
<td>42.2</td>
<td>59.1</td>
<td>0.61</td>
</tr>
<tr>
<td>CoMo/γ-Al₂O₃-1</td>
<td>33.6</td>
<td>54.8</td>
<td>0.52</td>
</tr>
<tr>
<td>Co/Mo-S/δ-γ-Al₂O₃</td>
<td>39.8</td>
<td>46.4</td>
<td>0.81</td>
</tr>
<tr>
<td>CoMo/SiO₂</td>
<td>10.2</td>
<td>9.8</td>
<td>1.04</td>
</tr>
<tr>
<td>CoMo/Al₂O₃ (industrial)</td>
<td>11.0</td>
<td>11.0</td>
<td>1.00</td>
</tr>
<tr>
<td>CoMo/Al₂O₃</td>
<td>62.0</td>
<td>98.0</td>
<td>0.25</td>
</tr>
<tr>
<td>Sn-CoMo/Al₂O₃</td>
<td>11.16</td>
<td>24.5</td>
<td>0.42</td>
</tr>
<tr>
<td>CoMo/Al₂O₃</td>
<td>31.0</td>
<td>47.0</td>
<td>0.58</td>
</tr>
<tr>
<td>K-CoMo/Al₂O₃</td>
<td>25.0</td>
<td>47.0</td>
<td>0.45</td>
</tr>
<tr>
<td>K-CoMo/Al₂O₃</td>
<td>10.0</td>
<td>26.0</td>
<td>0.35</td>
</tr>
<tr>
<td>B-CoMo/Al₂O₃</td>
<td>24.0</td>
<td>37.0</td>
<td>0.59</td>
</tr>
</tbody>
</table>

The HDS/HYDO selectivities linearly depend on the number of CoMo sites on the slab edges.

P. Nikulshin et al. // J. Catalysis 312 (2014) 152
During DBT HDS, the highest TOF/ value is achieved at a minimal $(\text{Co/Mo})_{\text{edge}}$ ratio (0.3 – 0.4) when the Co atoms are located on the S-edge and when the active phase is short.

**Activity of CoMo catalysts in DBT and 4,6-DMDBT HDS**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>DBT</th>
<th>4,6-DMDBT</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>23.9</td>
<td>4.4</td>
<td>Present work</td>
</tr>
<tr>
<td>Co$_3$[EDTA]-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>18.8</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>Industrial catalyst</td>
<td>0.4</td>
<td>-</td>
<td>S.T. Oyama et al.</td>
</tr>
<tr>
<td>Industrial catalyst</td>
<td>0.4</td>
<td>0.1</td>
<td>M. Kouzu et al.</td>
</tr>
<tr>
<td>CoMo/Al$_2$O$_3$</td>
<td>10.8</td>
<td>1.4</td>
<td>Lee et al.</td>
</tr>
<tr>
<td>CoMo-S/γ-Al$_2$O$_3$</td>
<td></td>
<td>0.8</td>
<td>Laurenti et al.</td>
</tr>
<tr>
<td>CoMoS-S/γT-Al$_2$O$_3$</td>
<td></td>
<td>1.3</td>
<td>J. Catalysis 297 (2013) 165</td>
</tr>
<tr>
<td>CoMoS-S/δ-Al$_2$O$_3$</td>
<td></td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>CoMoS-acac/γ-Al$_2$O$_3$</td>
<td></td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>CoMoS-acac/γT-Al$_2$O$_3$</td>
<td></td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>CoMoS-acac/δ-Al$_2$O$_3$</td>
<td></td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>
Deep diesel hydrotreating over Co₃[Chel]-Co₂Mo₁₀/Al₂O₃ catalysts

**Bench-scale flow reactor**
- Feedstock: SRGO&LCO (80/20)
- Catalyst: 10 cm³ in SiC
- P(H₂) = 4.0 MPa
- Temperature = 340 °C
- LHSV = 2.0 h⁻¹
- HTO = 500 NL/L

Dependence of S content in hydrogenated products of diesel HDT on effective Co content in CoMoS determined by XPS

*Nikulshin et. al. Patent of Russia*
Topics

1. Development of new sulfide catalysts
   1.1 New molecular precursors of active phases
   1.2 Effect of composition and morphology of active phase species on catalytic properties

2. Catalysts for deep hydrotreating of oil fractions
   2.1 Trimetallic NiCoMoS catalysts with enhanced HDS & HYD activities
   2.2 Spillover effect in catalysis by sulfides
   2.3 NiW/Al₂O₃ catalysts prepared with heteropolycompounds

3. Catalysts for selective hydrodesulfurization of FCC gasolines
   3.1 Trimetallic KCoMoS catalysts with improved HDS/HYDO selectivity

4. Catalysts for co-hydrotreating of diesel and vegetable oil
   4.1 Carbon-covered supports for sulfide catalysts
The aim of this work was to investigate the co-promotion effect in NiCoMo/Al₂O₃ catalysts based on Co₂Mo₁₀-heteropolyacid and nickel citrate.
## Composition of prepared Co$_x$-Co$_2$Mo$_{10}$/Al$_2$O$_3$ and Ni$_x$-Co$_2$Mo$_{10}$/Al$_2$O$_3$ catalysts

### Incipient pore-volume impregnation

- **Co$_2$Mo$_{10}$HPA** (T=40°C, water solution)
- **Al$_2$O$_3$**
  - $S_g = 220$ m$^2$/g, $V_p = 0.60$ cm$^3$/g, $D_p = 6.0$ nm
- Dried, 120°C (5 h)

### Catalysts Preparation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Atomic ratio</th>
<th>Content in the catalyst (wt. %)</th>
<th>Specific surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Al$_2$O$_3$</td>
<td>-</td>
<td>10.2</td>
<td>134</td>
<td>0.31</td>
<td>56</td>
</tr>
<tr>
<td>Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>0.17</td>
<td>10.1 1.3</td>
<td>115</td>
<td>0.25</td>
<td>56</td>
</tr>
<tr>
<td>Co$_1$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>0.25</td>
<td>9.9 2.0</td>
<td>105</td>
<td>0.21</td>
<td>56</td>
</tr>
<tr>
<td>Co$_3$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>0.35</td>
<td>10.0 3.3</td>
<td>90</td>
<td>0.18</td>
<td>56/38</td>
</tr>
<tr>
<td>Co$_6$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>0.45</td>
<td>10.0 5.0</td>
<td>75</td>
<td>0.14</td>
<td>56/38</td>
</tr>
<tr>
<td>Ni$_1$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>0.16</td>
<td>10.2 1.3 0.8</td>
<td>111</td>
<td>0.26</td>
<td>56</td>
</tr>
<tr>
<td>Ni$_3$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>0.14</td>
<td>9.9 1.3 2.0</td>
<td>92</td>
<td>0.18</td>
<td>56/38</td>
</tr>
<tr>
<td>Ni$_6$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>0.11</td>
<td>10.1 1.3 3.8</td>
<td>80</td>
<td>0.16</td>
<td>56/38</td>
</tr>
</tbody>
</table>

---

Dependence of effective amount of Co and Ni particles on Co(Ni)/(Co+Ni+Mo) promotion degree

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co percentage in CoMoS</th>
<th>CoS₈</th>
<th>Co²⁺</th>
<th>NiMoS</th>
<th>NiS</th>
<th>Ni²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co₂Mo₁₀/Al₂O₃</td>
<td>63</td>
<td>2</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co₁-Co₂Mo₁₀/Al₂O₃</td>
<td>55</td>
<td>9</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co₃-Co₂Mo₁₀/Al₂O₃</td>
<td>50</td>
<td>15</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co₆-Co₂Mo₁₀/Al₂O₃</td>
<td>31</td>
<td>31</td>
<td>38</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni₁-Co₂Mo₁₀/Al₂O₃</td>
<td>62</td>
<td>3</td>
<td>35</td>
<td>47</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td>Ni₃-Co₂Mo₁₀/Al₂O₃</td>
<td>63</td>
<td>2</td>
<td>35</td>
<td>44</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>Ni₆-Co₂Mo₁₀/Al₂O₃</td>
<td>62</td>
<td>2</td>
<td>36</td>
<td>25</td>
<td>40</td>
<td>35</td>
</tr>
</tbody>
</table>

XPS Ni2p spectra recorded for Ni₃-Co₂Mo₁₀/Al₂O₃ catalyst
Rate constants in DBT HDS vs promotion degree and the effective amount of active phase species

For both series of the catalysts, HDS activity passed through maximum with increasing Ni or Co. Maximal rate constants were reached at 0.33 of Co(Ni)/(Co+Ni+Mo).

At equal content of Co in CoMoS and sum of the Co and Ni in the NiCoMoS phase, the Ni$_x$-Co$_2$Mo$_{10}$S/Al$_2$O$_3$ catalysts were more active.

What are the reasons of the changes in the activities of the promoted (Ni)CoMoS catalysts?
TOF values in DBT HDS on prepared Co$_x$-Co$_2$Mo$_{10}$/Al$_2$O$_3$ and Ni$_x$-Co$_2$Mo$_{10}$/Al$_2$O$_3$ catalysts

For MoS$_2$/Al$_2$O$_3$ catalysts:

$$\text{TOF}_{\text{edge}} \times [\text{Mo}^{IV\text{edge}}] = \text{TOF}_{\text{Mo}} \times [\text{Mo}]$$

For CoMoS$_2$/Al$_2$O$_3$ catalysts:

$$\text{TOF}_{\text{edge}} \times [\text{Mo}^{IV\text{edge}}] = \text{TOF}_{\text{Mo}} \times [\text{Mo}] + \text{TOF}_{\text{Co}} \times [\text{Co}]$$

For NiCoMoS$_2$/Al$_2$O$_3$ catalysts:

$$\text{TOF}_{\text{edge}} \times [\text{Mo}^{IV\text{edge}}] = \text{TOF}_{\text{Mo}} \times [\text{Mo}] + \text{TOF}_{\text{Co}} \times [\text{Co}] + \text{TOF}_{\text{Ni}} \times [\text{Ni}]$$

### Content of active sites and TOF values ($\times 10^{-4}$ s$^{-1}$) in HDS of DBT

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Mo$^{IV\text{edge}}$ site (10$^{20}$ at. g$^{-1}$)</th>
<th>(Co/Mo)$_{\text{edge}}$</th>
<th>(Ni/Mo)$_{\text{edge}}$</th>
<th>TOF$_{\text{edge}}$</th>
<th>TOF$_{\text{Mo}}$</th>
<th>TOF$_{\text{Co}}$</th>
<th>TOF$_{\text{Ni}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Al$_2$O$_3$</td>
<td>1.26</td>
<td>-</td>
<td>-</td>
<td>0.63</td>
<td>0.63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>1.68</td>
<td>0.43</td>
<td>-</td>
<td>3.5</td>
<td>0.63</td>
<td>7.3</td>
<td>-</td>
</tr>
<tr>
<td>Co$_{1-x}$Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>1.48</td>
<td>0.68</td>
<td>-</td>
<td>5.1</td>
<td>0.63</td>
<td>6.9</td>
<td>-</td>
</tr>
<tr>
<td>Co$_3$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>1.66</td>
<td>1.09</td>
<td>-</td>
<td>7.1</td>
<td>-</td>
<td>6.4</td>
<td>-</td>
</tr>
<tr>
<td>Co$_6$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>1.35</td>
<td>1.16</td>
<td>-</td>
<td>7.1</td>
<td>-</td>
<td>6.1</td>
<td>-</td>
</tr>
<tr>
<td>Ni$_{1-x}$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>1.64</td>
<td>0.44</td>
<td>0.23</td>
<td>7.5</td>
<td>0.63</td>
<td>7.3</td>
<td>17.9</td>
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<tr>
<td>Ni$_3$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>1.66</td>
<td>0.44</td>
<td>0.57</td>
<td>9.8</td>
<td>-</td>
<td>7.3</td>
<td>11.6</td>
</tr>
<tr>
<td>Ni$_6$-Co$<em>2$Mo$</em>{10}$/Al$_2$O$_3$</td>
<td>1.66</td>
<td>0.45</td>
<td>0.64</td>
<td>9.7</td>
<td>-</td>
<td>7.3</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Topics

1. Development of new sulfide catalysts
   1.1 New molecular precursors of active phases
   1.2 Effect of composition and morphology of active phase species on catalytic properties

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The use of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and Ni(Citr) for preparation of NiWS/Al$_2$O$_3$ catalysts

Simultaneous use of PW$_{12}$HPA and Ni(Citr) led to formation of NiWS phase contained much more Ni than in the references.

Both NiW reference catalysts had active sites with lower TOF than their counterparts from PW$_{12}$HPA and Ni(Citr).

Better dispersion of NiWS species and beneficial role of coke formed from citric molecules during catalyst sulfidation.

Rate constants of the DBT HDS over NiWS/Al$_2$O$_3$ catalysts

3D dependence of the TOF number in DBT HDS, naphthalene HYD and quinoline HDN over $\lambda$-Ni-CA-PW/Al$_2$O$_3$ catalysts on the average length of the NiWS phase species and (Ni/W)$_{\text{edge}}$.
Testing of catalytic properties in VGO hydrotreating

**Bench-scale flow reactor**

- Catalyst: 15 cm³ in SiC
- P(H₂) = 5.0 MPa, T = 360-390 °C
- LHSV = 0.5 – 1.5 h⁻¹, HTO = 800 NL/L

**Characteristics of VGO**

<table>
<thead>
<tr>
<th>Item</th>
<th>VGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation (°C)</td>
<td>350 – 500</td>
</tr>
<tr>
<td>Density at 20 °C (g/cm³)</td>
<td>901</td>
</tr>
<tr>
<td>Content (wt. %)</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.7</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.089</td>
</tr>
<tr>
<td>Polycyclic aromatics</td>
<td>9.2</td>
</tr>
</tbody>
</table>

**Conditions and results of VGO hydrotreating over NiWS/Al₂O₃ catalyst**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>LHSV (h⁻¹)</th>
<th>P (MPa)</th>
<th>HTO (NL/L)</th>
<th>Sulfur (ppm)</th>
<th>Nitrogen (ppm)</th>
<th>PACs (%) wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiWS/Al₂O₃</td>
<td>360</td>
<td>0.5</td>
<td>5.0</td>
<td>800</td>
<td>120</td>
<td>147</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>1.0</td>
<td>5.0</td>
<td>800</td>
<td>342</td>
<td>264</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>1.0</td>
<td>5.0</td>
<td>800</td>
<td>60</td>
<td>82</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Topics

1. Development of new sulfide catalysts
   1.1 New molecular precursors of active phases
   1.2 Effect of composition and morphology of active phase species on catalytic properties

2. Catalysts for deep hydrotreating of oil fractions
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Hydrotreating processes in oil refinery

Crude Oil after Desalting

Atm Dist

Vac Dist

SRGO

VGO

Coking

Gasoline fractions

Deep hydrotreating

Gasoline

Vac Dist

Deep hydrotreating

Deep hydrotreating

Diesel fuel

Deep hydrotreating

Selective hydrotreating

FCC

Typical components of regular gasoline

FCC gasoline

Light Naphtha

Alkylate

Reformate

Others

<table>
<thead>
<tr>
<th>Gasoline blendstocks</th>
<th>Percent of pool volume</th>
<th>Percent of pool sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC naphtha</td>
<td>36</td>
<td>98</td>
</tr>
<tr>
<td>Reformate</td>
<td>34</td>
<td>—</td>
</tr>
<tr>
<td>Alkylate</td>
<td>12</td>
<td>—</td>
</tr>
<tr>
<td>Isomerate</td>
<td>5</td>
<td>—</td>
</tr>
<tr>
<td>Butanes</td>
<td>5</td>
<td>—</td>
</tr>
<tr>
<td>Light straight-run naphtha</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Hydrocracked naphtha</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>MTBE</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Coker naphtha</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Towards control of selectivity factor HDS/HYDO in FCC gasoline HDT: background

[Co(Ligand)]-Co$_2$Mo$_{10}$Al$_2$O$_3$ catalysts

HYDO
CoMo corner site

HDS
CoMo edge site
## Preparation of KCoMoS/Al₂O₃ catalysts and their textural properties

**PMo₁₂HPA**

\[ \text{Al}_2\text{O}_3 \]

\( S_g = 220 \text{ m}^2/\text{g}, \ V_p = 0.747 \text{ cm}^3/\text{g} \)

**Citric acid**

**KOH**

**CoCO₃**

**Kₓ-(CA)-PMo₁₂/Al₂O₃**

in oxide form

**Co₆(CA)-Kₓ-PMo₁₂/Al₂O₃**

in oxide form

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal content (% wt.)</th>
<th>Textural characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMo₁₂/Al₂O₃</td>
<td>12 - -</td>
<td>169 0.30 67</td>
</tr>
<tr>
<td>K₅%(CA)-PMo₁₂/Al₂O₃</td>
<td>12 - 5</td>
<td>92 0.28 67</td>
</tr>
<tr>
<td>K₁₀%(CA)-PMo₁₂/Al₂O₃</td>
<td>12 - 10</td>
<td>73 0.27 67</td>
</tr>
<tr>
<td>K₁₅%(CA)-PMo₁₂/Al₂O₃</td>
<td>12 - 15</td>
<td>47 0.19 67</td>
</tr>
<tr>
<td>Co₆(CA)-PMo₁₂/Al₂O₃</td>
<td>12 3.7 -</td>
<td>178 0.36 67</td>
</tr>
<tr>
<td>Co₆(CA)-K₅%-PMo₁₂/Al₂O₃</td>
<td>12 3.7 5</td>
<td>111 0.35 67</td>
</tr>
<tr>
<td>Co₆(CA)-K₇.5%-PMo₁₂/Al₂O₃</td>
<td>12 3.7 7.5</td>
<td>94 0.34 59</td>
</tr>
<tr>
<td>Co₆(CA)-K₁₀%-PMo₁₂/Al₂O₃</td>
<td>12 3.7 10</td>
<td>58 0.23 59</td>
</tr>
<tr>
<td>Co₆(CA)-K₁₅%-PMo₁₂/Al₂O₃</td>
<td>12 3.7 15</td>
<td>23 0.10 59</td>
</tr>
</tbody>
</table>
Physical-chemical properties of synthesized catalysts: NH$_3$-TPD and Raman spectroscopy

<table>
<thead>
<tr>
<th>K amount, % wt.</th>
<th>Desorbed NH$_3$, μmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>379</td>
</tr>
<tr>
<td>5</td>
<td>52</td>
</tr>
<tr>
<td>7.5</td>
<td>18</td>
</tr>
<tr>
<td>15</td>
<td>8</td>
</tr>
</tbody>
</table>

Potassium decreases the amount of acidic sites on the catalyst surface.

Poymolybdate entities are saved on the oxidic catalysts within investigated potassium content (5-15 wt. %).

Polymolybdate entities are formed

## Physical-chemical properties of synthesized (K)Mo and (K)CoMo catalysts: XPS and TEM

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CoMoS</th>
<th>Co(_9)S(_8)</th>
<th>Co(^{2+})</th>
<th>MoS(_2)</th>
<th>MoS(_{xO_y})</th>
<th>Mo(^{6+})</th>
<th>(\bar{L}) (nm)</th>
<th>(\bar{N})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMo(_{12}/)Al(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>70</td>
<td>10</td>
<td>20</td>
<td>3.4</td>
<td>1.6</td>
</tr>
<tr>
<td>K(<em>5)%PMo(</em>{12}/)Al(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>7</td>
<td>12</td>
<td>3.9</td>
<td>1.6</td>
</tr>
<tr>
<td>K(<em>{10})%PMo(</em>{12}/)Al(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>82</td>
<td>8</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K(<em>{15})%PMo(</em>{12}/)Al(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>86</td>
<td>7</td>
<td>7</td>
<td>5.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Co(CA)-PMo(_{12}/)Al(_2)O(_3)</td>
<td>57</td>
<td>13</td>
<td>30</td>
<td>70</td>
<td>16</td>
<td>14</td>
<td>3.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Co(CA)-K(<em>5)%PMo(</em>{12}/)Al(_2)O(_3)</td>
<td>63</td>
<td>12</td>
<td>25</td>
<td>74</td>
<td>14</td>
<td>12</td>
<td>4.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Co(CA)-K(<em>7.5)%PMo(</em>{12}/)Al(_2)O(_3)</td>
<td>66</td>
<td>10</td>
<td>24</td>
<td>74</td>
<td>12</td>
<td>14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co(CA)-K(<em>10)%PMo(</em>{12}/)Al(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Co(CA)-K(<em>15)%PMo(</em>{12}/)Al(_2)O(_3)</td>
<td>74</td>
<td>5</td>
<td>21</td>
<td>82</td>
<td>10</td>
<td>10</td>
<td>6.3</td>
<td>2.4</td>
</tr>
</tbody>
</table>

**Potassium improves:**

- the sulfidation degree of active metals with more selective formation of CoMoS phase;
- the growth of average slab length

**Potassium partially insert in sulfide slab with changing the nature of active sites and probably with formation of new type of active sites.**
Hydrotreating of model gasoline

**Conditions:**
Bench scale flow reactor
Feedstock: \( n \)-hexene-1 (36 wt.%), thiophene (0.1 wt.% S), \( n \)-heptane (solvent)
\( t = 220^\circ C \)
\( P = 1.5 \) MPa
LHSV = 5.0 h\(^{-1}\);
\( H_2 / \text{feedstock} = 100 \) NL/L;

\[ L = 3.8 \text{ nm} \]
\[ N = 1.5 \]

---

**Graphs:**
- \( K_x \)-PMo\(_{12}/Al_2O_3 \)
- \( Co(\text{CA})-K_x\)-PMo\(_{12}/Al_2O_3 \)
Hydrotreating of model gasoline

**Conditions:**
Bench scale flow reactor
Feedstock:  
- n-hexene-1 (36 wt.%),
- thiophene (0.1 wt.% S),
- n-heptane (solvent)

- $t = 220^\circ$C
- $P = 1.5$ MPa
- $LHSV = 5.0$ h$^{-1}$;
- $H_2$/feedstock = 100 NL/L;

$L = 3.8$ nm
$N = 1.5$

- $K_x$-PMo$_{12}$/Al$_2$O$_3$
- Co(CA)-$K_x$-PMo$_{12}$/Al$_2$O$_3$
**Hydrotreating of model gasoline**

**Conditions:**
Bench scale flow reactor
Feedstock:  
- $n$-hexene-1 (36 wt.%),
- thiophene (0.1 wt.% S),
- $n$-heptane (solvent)

$t = 220^\circ\text{C}$
$P = 1.5 \text{ MPa}$
$LHSV = 5.0 \text{ h}^{-1}$;
$\frac{\text{H}_2}{\text{feedstock}} = 100 \text{ NL/L};$

$\bar{L} = 6.3 \text{ nm}$
$\bar{N} = 2.4$
Hydrotreating of model gasoline

- Potassium increases the sulfidation degree of metals, content of CoMoS phase and average slab length.
- Promoting catalysts by potassium leads to the partial poisoning the active sites.

\[
\text{Conversion} = \frac{\text{Conversion}}{\text{Initial Conversion}}
\]

\[
\text{Selectivity factor} = \frac{\text{Selectivity}}{\text{Initial Selectivity}}
\]
Hydrotreating of model gasoline

Promoting catalysts with potassium leads to the partial poisoning of the active sites.

Potassium increases the sulfidation degree of metals, content of CoMoS phase and average slab length.

- **Promoting catalysts with potassium leads to the partial poisoning of the active sites.**
Hydrotreating of model gasoline

- Potassium increases the sulfidation degree of metals, content of CoMoS phase and average slab length.
- Promoting catalysts with potassium leads to the partial poisoning of the active sites.
- Olefin HYD is more sensitive to potassium than HDS reaction.

Heavy FCC gasoline hydrotreating over KCoPMo$_{12}$/Al$_2$O$_3$ catalysts

**FCC gasoline**

**Splitter**

28 - 110°C

RON = 91.2
S cont. = 12.0 ppm
Olefins = 22.6 wt.

110 - FBP°C

RON = 91.7
S cont. = 92.1 ppm
Olefins = 13.5 wt.

**Merox**

**Blended product**

RON = 91.0
S cont. = 13.0 ppm
Olefins = 19.6 wt.

**Selective HDS**

RON = 91.6
S cont. = 14.0 ppm
Olefins = 12.9 wt.

HYDO = 4.4 %
HDS = 84.8 %

Saving octane number!
Topics

1. Development of new sulfide catalysts
   1.1 New molecular precursors of active phases
   1.2 Effect of composition and morphology of active phase species on catalytic properties

2. Catalysts for deep hydrotreating of oil fractions
   2.1 Trimetallic NiCoMoS catalysts with enhanced HDS & HYD activities
   2. NiW/Al₂O₃ catalysts prepared with heteropolycompounds

3. Catalysts for selective hydrodesulfurization of FCC gasolines
   3.1 Trimetallic KCoMoS catalysts with improved HDS/HYDO selectivity

4. Catalysts for co-hydrotreating of diesel and vegetable oil
   4.1 Carbon-covered supports for sulfide catalysts
Production of biofuels

Co-processing of bio- and oil raw materials

Wood biomass

Triglycerides of fatty acids

Pyrolysis

Re-esterification CH₃OH

Bio-oil

New fuels

Green diesel Bio-diesel

Consumption of energy by transports (Shell)

Fuels from oil

Bio-fuels

Amount

Publication evolution by Scopus database

S < 0.1 ppm

CN > 80 p.

O = absence

Stable

S < 0.1 ppm

CN 50 p.

O = 11 wt. %

Not stable

4,0 mln. L/year

30%
Anderson type XMo₆HPA
Catalytic properties: guaiacol HDO

Guaiacol HDO

Conditions:

Bench scale flow reactor
Feedstock: guaiacol (3 wt.%), DMDS (0.6 wt.% S), toluene (solvent)

\[ k_{\text{HDO}} = - \frac{F}{W} \ln(1 - x_{\text{HDO}}) \]

\[ D_{\text{Dea}}_{\text{HDO}} = \left( 1 - \frac{x_{\text{HDO}}^{\text{Stat}}}{x_{\text{HDO}}^{\text{Init}}} \right) \times 100\% \]

\[ \text{Activity} \]

\[ \text{Deactivation} \]

TOS = 15 h

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_{\text{HDO}} × 10³, mol/(g·h)</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Dea, %</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Effect of support acidity of CoMo catalysts on their activity in guaiacol HDO

<table>
<thead>
<tr>
<th>Support</th>
<th>Content carbon, % wt.</th>
<th>acid sites (μmol NH₃/g)</th>
<th>Textural properties S_{BET}, m²/g</th>
<th>V_p, cm³/g</th>
<th>R_{av}, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>200</td>
<td>208</td>
<td>0.62</td>
<td>48</td>
</tr>
<tr>
<td>Al₂O₃-ZSM-5</td>
<td>-</td>
<td>233</td>
<td>240</td>
<td>0.67</td>
<td>48</td>
</tr>
<tr>
<td>Al₂O₃-BETA</td>
<td>-</td>
<td>308</td>
<td>263</td>
<td>0.66</td>
<td>48</td>
</tr>
<tr>
<td>C₆/Al₂O₃</td>
<td>5.6</td>
<td>142</td>
<td>184</td>
<td>0.49</td>
<td>48</td>
</tr>
<tr>
<td>Sibunit (C)</td>
<td>99.4</td>
<td>10</td>
<td>233</td>
<td>0.41</td>
<td>19</td>
</tr>
</tbody>
</table>

- CoMo catalysts supported on alumina modified carriers were prepared
- Catalysts were tested in guaiacol HDO reaction

Co(CA)-PMo₁₂HPA catalysts

Deactivation vs support acidity

P. Nikulshin et al. Catal Ind 6 (2014) 338
Activity of Co-PMo/C/Al₂O₃ catalysts in oleic acid HDO

Co-PMo/Cₓ/Al₂O₃ catalyst

Heptadecene

Heptadecane

C₁₇H₃₄

C₁₇H₃₂

C₁₇H₃₆

Carbon content in C/Al₂O₃ (% wt.)

Carbon content in C/Al₂O₃ (% wt.)

Selectivity C₁₈/ C₁₇

Deactivation degree (%)

Oleic acid

Octadecanol

Octadecanal

Octadecanethiol

Octadecenol

Octadecenal

HDO pathway

DEC pathway

### Characteristics of used feedstock

<table>
<thead>
<tr>
<th>Item</th>
<th>SRGO (100 wt.)</th>
<th>SRGO (85 % wt.) + SO (15 % wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane number, p.</td>
<td>49</td>
<td>50</td>
</tr>
<tr>
<td>Total sulfur content, ppm</td>
<td>9209</td>
<td>8031</td>
</tr>
<tr>
<td>Density at 20 °C, kg/m³</td>
<td>0.837</td>
<td>0.849</td>
</tr>
<tr>
<td>Distillation:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- IBP</td>
<td>186</td>
<td>190</td>
</tr>
<tr>
<td>- 10% at temperature</td>
<td>217</td>
<td>217</td>
</tr>
<tr>
<td>- 50% at temperature</td>
<td>278</td>
<td>284</td>
</tr>
<tr>
<td>- 90% at temperature</td>
<td>344</td>
<td>364</td>
</tr>
<tr>
<td>- 95% at temperature</td>
<td>365</td>
<td>372</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>75</td>
<td>74</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>-6.5</td>
<td>-5.5</td>
</tr>
<tr>
<td>Iodine number, g I₂/100 g</td>
<td>1.5</td>
<td>20.2</td>
</tr>
</tbody>
</table>

### Conditions:

- \( t = 280 - 380 \, ^\circ\text{C} \); \( P = 4.0 \, \text{MPa} \);
- \( \text{LHSV} = 1.0 – 4.0 \, \text{h}^{-1} \);
- \( \text{H}_2/\text{feed} = 500 \, \text{nL/L} \); \( V_{\text{cat}} = 15 \, \text{cm}^3 \)

Mixture with 5, 10 and 15 % of sunflower oil with SRGO were used.

\[
 k_{\text{HDS}} = \frac{C_S^{1-n} - C_{S}^{01-n}}{\tau \cdot (1 - n)}
\]
Co-hydrotreating SRGO with sunflower oil (SO) in bench-scale flow reactor

**Co-PMo_12/Al_2O_3 catalyst**

- SRGO (85%) + SO (15%)
- SRGO (100%)

**Dependence of S content in the hydrogenated products on time contact**

**Necessary temperature increase (ΔT) to produce diesel with S = 50 ppm from SRGO and SO 15%**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ΔT for 50 ppm S (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-PMo/Al_2O_3</td>
<td>+19</td>
</tr>
<tr>
<td>Ni-PMo/Al_2O_3</td>
<td>+3</td>
</tr>
<tr>
<td>Ni-PMo/C_2/Al_2O_3</td>
<td>-</td>
</tr>
</tbody>
</table>
Co(Ni)-PMo/Sup catalysts in co-hydrotreating of SRGO with sunflower oil: accelerated deactivation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Sulfur content (ppm)</th>
<th>Cetane number</th>
<th>Pour point (°C)</th>
<th>Deactivation HDS (%)</th>
<th>Coke content (% wt.)</th>
<th>Deactivation HDS (%) SRGO + LCO + LCGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-PMo/Al₂O₃</td>
<td>170</td>
<td>55.0</td>
<td>-0.5</td>
<td>318</td>
<td>7.3</td>
<td>15-30</td>
</tr>
<tr>
<td>Ni-PMo/Al₂O₃</td>
<td>70</td>
<td>55.0</td>
<td>-0.5</td>
<td>263</td>
<td>6.1</td>
<td>-</td>
</tr>
<tr>
<td>Ni-PMo/C₂/Al₂O₃</td>
<td>50</td>
<td>55.0</td>
<td>-0.5</td>
<td>184</td>
<td>5.7</td>
<td>-</td>
</tr>
</tbody>
</table>

T = 340 °C, P = 4.0 MPa, LHSV = 2.0 h⁻¹, HTO = 500 nL/L, Feedstock: SRGO+SO

T = 380 °C, P = 1.0 MPa, OCPIC = 2.0 h⁻¹, HTO = 150 nL/L, Feedstock: SRGO

R1: T = 340 °C, P = 4.0 MPa, LHSV = 2.0 h⁻¹, HTO = 500 nL/L, Feedstock: SRGO+SO

R2: T = 340 °C, P = 4.0 MPa, LHSV = 2.0 h⁻¹, HTO = 500 nL/L, Feedstock: SRGO+SO

Instead of conclusions

\[
\text{TOF}_{XMS} = \mathcal{A}(\text{Mor}(N, L), (X/M)_{\text{edge}}) \times \mathcal{A}(P, T) \times \mathcal{A}(\text{Spillover})
\]

**Principals of molecular designing of hydrotreating catalysts**

<table>
<thead>
<tr>
<th>Hydroprocessing</th>
<th>Active phase composition</th>
<th>Active phase morphology</th>
<th>Promoter degree of Mo(W)S₂ edges (Co(Ni)/Mo(W))&lt;sub&gt;edge&lt;/sub&gt;</th>
<th>Content of active sites Co(Ni)Mo(W) (% wt.)</th>
<th>Hydrogen activation and spillover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline hydrotreating</td>
<td>CoMoS, NiMoS</td>
<td>≥ 1, 2 – 4</td>
<td>0.1 – 0.6</td>
<td>&gt; 0.6</td>
<td>Necessary</td>
</tr>
<tr>
<td>FCC gasoline selective hydrotreating</td>
<td>KCoMoS</td>
<td>≥ 1, ≥ 5</td>
<td>0.9 – 1.0</td>
<td>0.6 – 0.9</td>
<td>Unnecessary</td>
</tr>
<tr>
<td>Diesel hydrotreating</td>
<td>CoMoS, NiMoS, NiCoMoS</td>
<td>≥ 1.6, 2 – 3</td>
<td>0.3 – 0.5</td>
<td>&gt; 1.2</td>
<td>Necessary</td>
</tr>
<tr>
<td>VGO hydrotreating</td>
<td>NiMoS, NiCoMoS, NiWS, NiMoWS</td>
<td>≥ 1.6, 3 – 4</td>
<td>0.3 – 0.7</td>
<td>&gt; 1.5</td>
<td>Necessary</td>
</tr>
<tr>
<td>Co-hydrotreating of diesel and vegetable oil</td>
<td>NiMoS, NiWS, NiMoWS</td>
<td>≥ 1.6, 2 – 3</td>
<td>0.3 – 0.7</td>
<td>&gt; 1.3</td>
<td>Necessary</td>
</tr>
</tbody>
</table>
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