

# **The active phases in a typical catalyst like hydrodesulphurization**

**Submitted by:**

**Vandana**

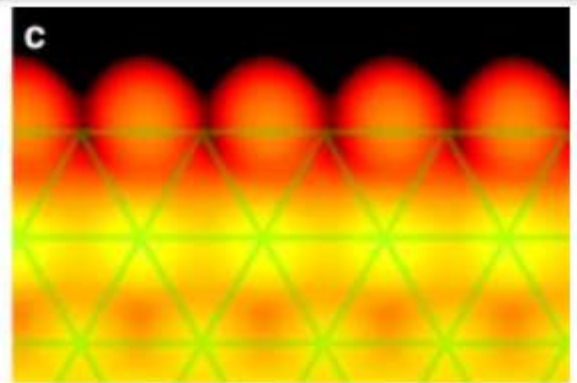
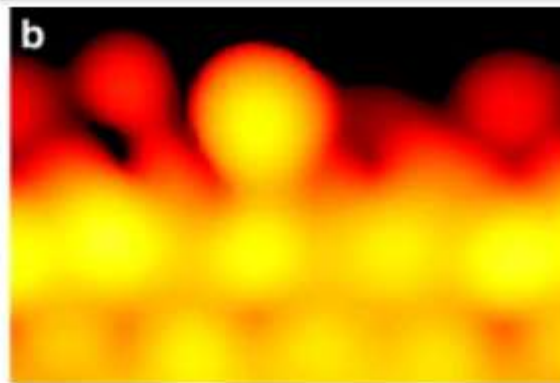
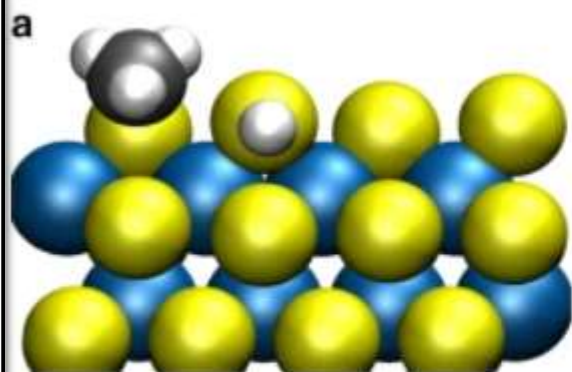
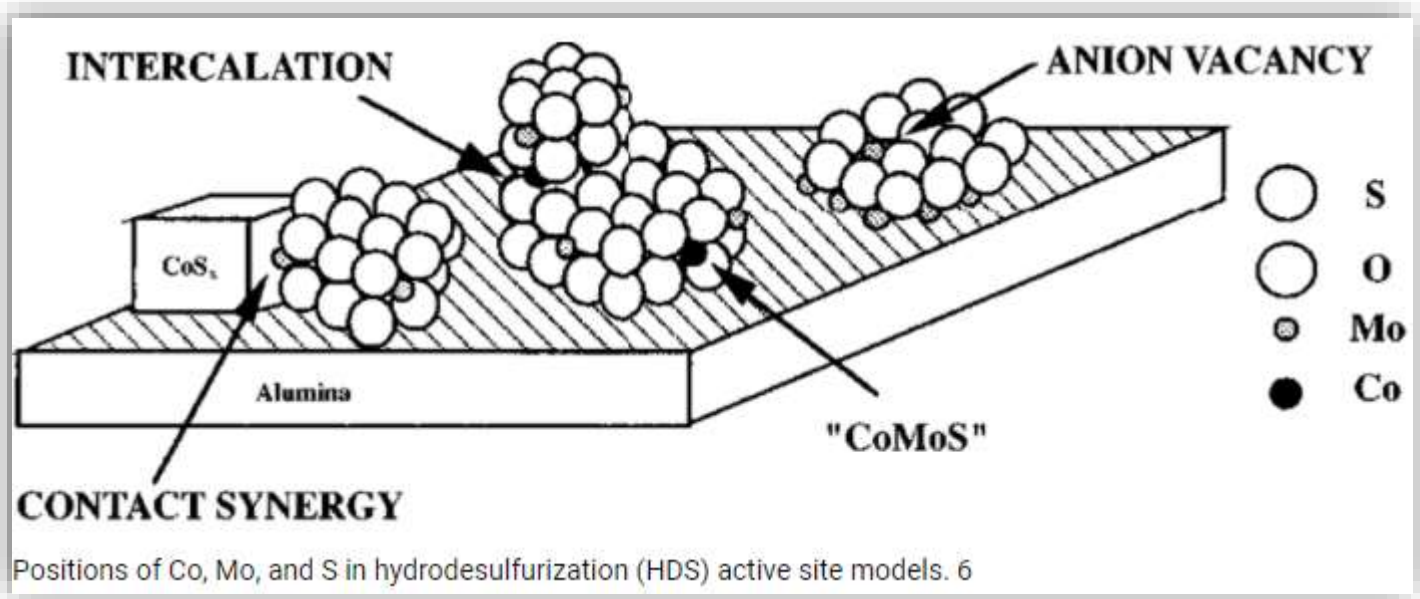
**Submitting to:**

**Prof. B.Viswanathan**

# Introduction..

- Hydrodesulphurization (HDS) and Hydrodenitrogenation (HDN) is a catalytic process typically used in the Oil & Gas and Refining industries to remove sulfur and nitrogen from natural gas or basic feed.
- It's a hydrogenolysis type of reaction and results in the cleavage of the **C-X** chemical bond by **H<sub>2</sub>**, where **C** is a carbon atom and **X** is a sulfur (S), nitrogen (N) or oxygen (O) atom.
- The net result of a hydrogenolysis reaction is the formation of **C-H** and **H-X** chemical bond.
- If we talk about industrial hydrodesulfurization unit, such as in a refinery, the hydrodesulfurization reaction takes place in a fixed-bed reactor at elevated temperature & pressure.





Thermodynamically preferred structure under the experimental desulfurization conditions

# Reaction MECHANISM INVOLVED IN Hydrodesulphurization (HDS)

- Dibenzyl thiophene (DBT) treated with the number of H<sub>2</sub> moles over Ni-Mo/Al<sub>2</sub>O<sub>3</sub> or Ni-Mo/TiO<sub>2</sub> catalyst.
- Yellowish product shows complete and only desulphurization using 2 moles of H<sub>2</sub> or we can say it is direct desulphurization.
- In green product we can get this **product (4-hydro dibenzyl thiophene)** depending upon the selectivity of catalyst. In which one benzene group is adopting saturation.
- On further exposure of no. of moles of H<sub>2</sub> we can get kinds of products also, like **cyclohexyl benzene (CHB)** or Bi-cyclohexyl (BCH).

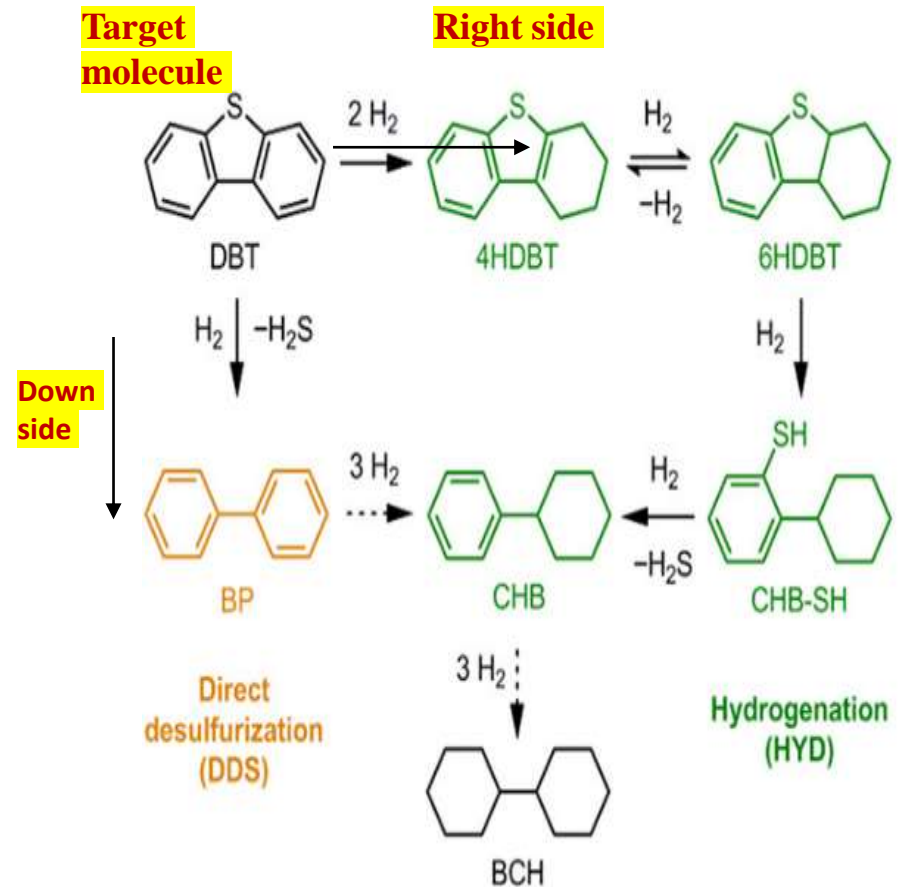
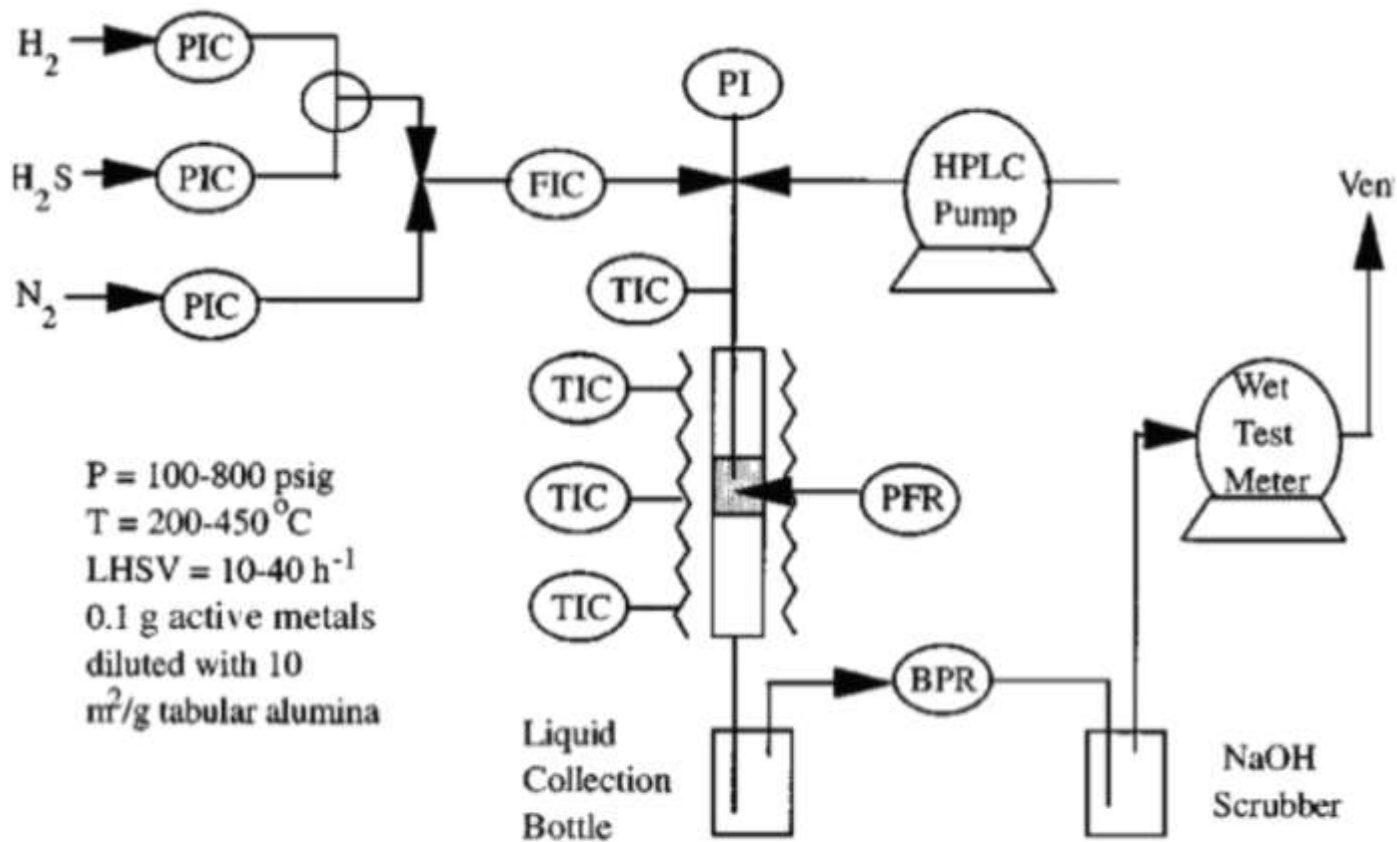


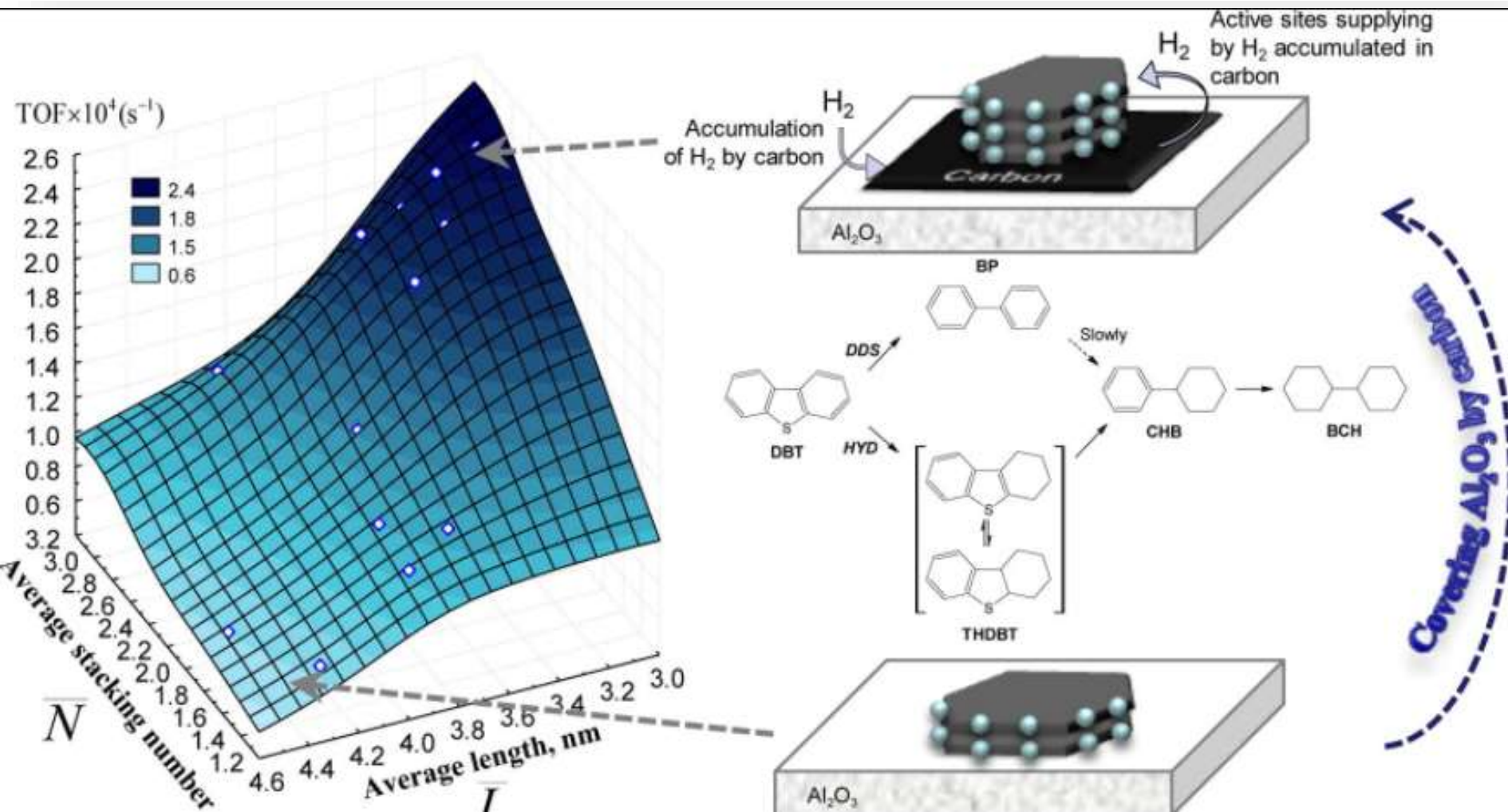
Fig.(1)



Pilot plant scale HDS catalytic reactor schematic. PIC ) pressure indicating controller, FIC ) flow indicating (mass flow controller), PFR ) plug flow reactor, BPR ) back pressure regulator, and PI ) pressure indicator (transducer)

## Catalyst SELECTION..

- Common combinations of active elements = Co-Mo, Ni-Mo and Ni-W supported on Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>.
- Catalyst selection is based on the application and desired activity/selectivity.
- Ni-Mo/TiO<sub>2</sub> = Good for HDS but few drawbacks such as low specific surface area, low mechanical strength, and low thermal stability.
- Ni-Mo/Al<sub>2</sub>O<sub>3</sub> = Shows high activity for HDS, HDN and HDA.
- Selectivity of heteroatom removal versus hydrogenation can be increased for alumina-supported catalysts by addition of phosphorous.
- Choosing proper catalyst particle size and shape, and pore system geometry is important.



Relationship between active phase morphology and catalytic properties of the carbon–alumina-supported Co(Ni)Mo catalysts in HDS

# Pore volume distribution of the catalysts..

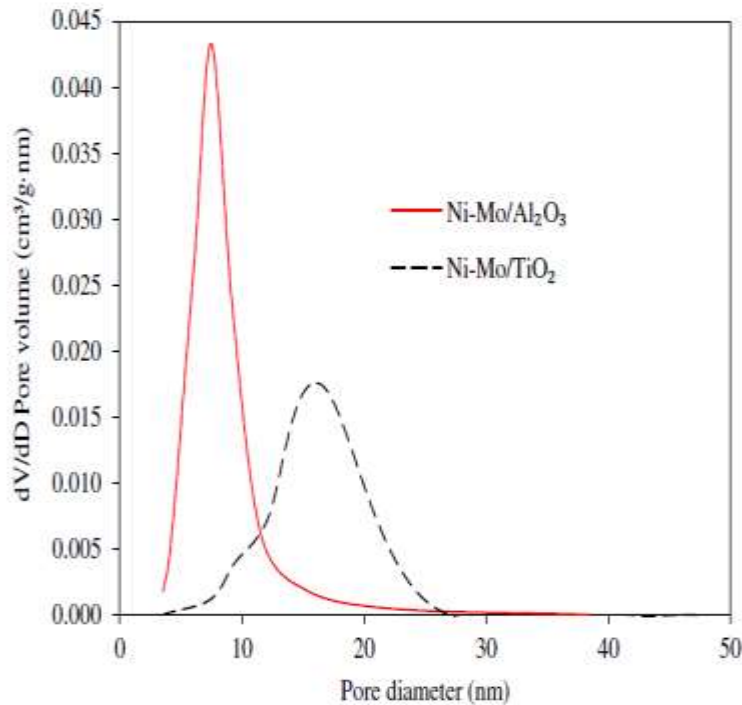


Fig. 1. Pore volume distribution of the catalysts by BJH(Barrett, Joyner, and Halenda )

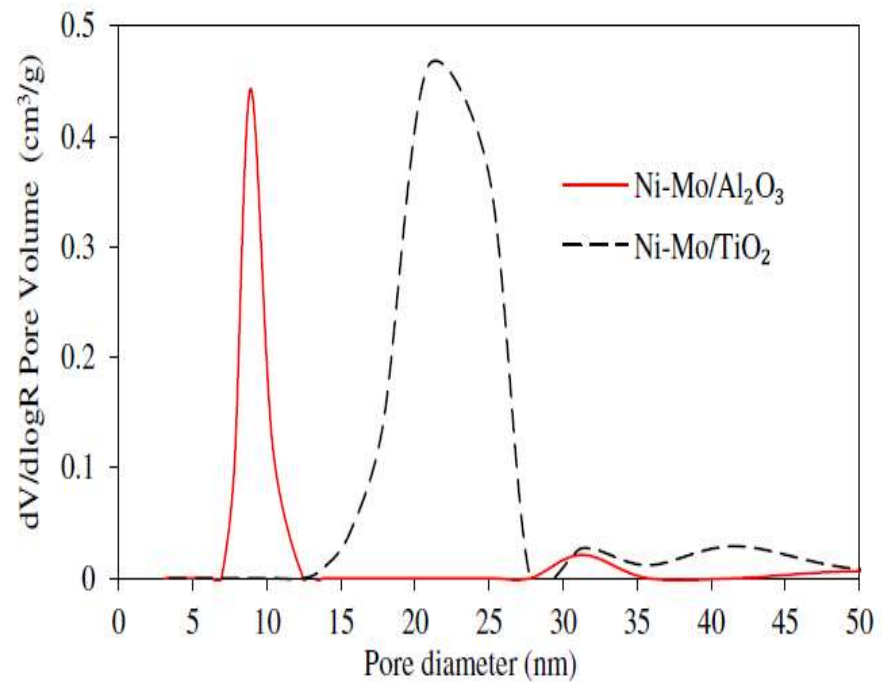


Fig. 2. Pore volume distribution of the catalysts (Hg porosimetry)

- The Al<sub>2</sub>O<sub>3</sub>-supported catalyst contained mesopores in the range of 5–14 nm in contrast.
- TiO<sub>2</sub>-supported catalyst that contained mesopores in the range of 8–25 nm.
- Higher activity of the Al<sub>2</sub>O<sub>3</sub>-supported catalyst may be caused by its greater surface area and the differences in mesopores size.



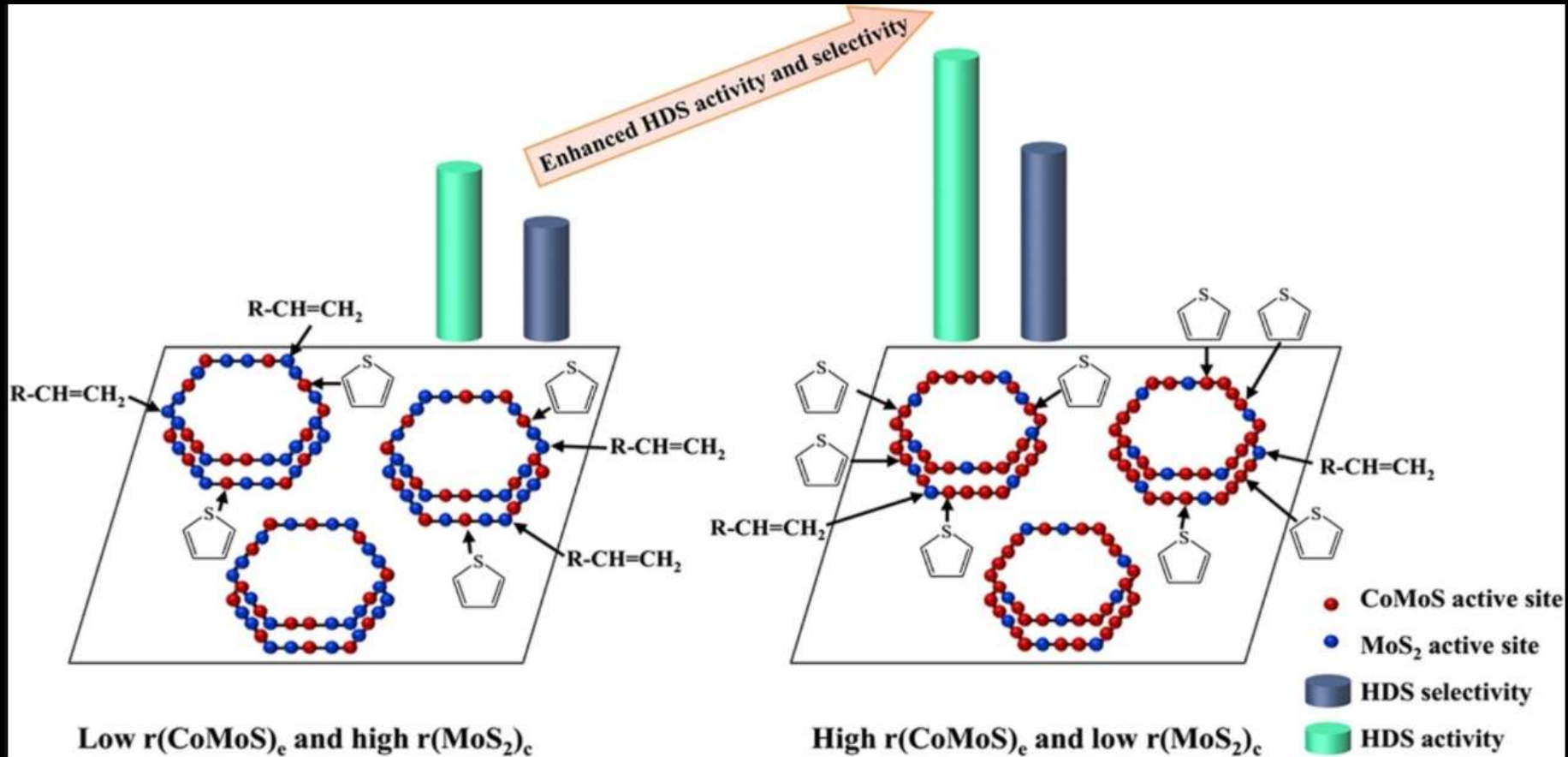
## Active phases in HDS

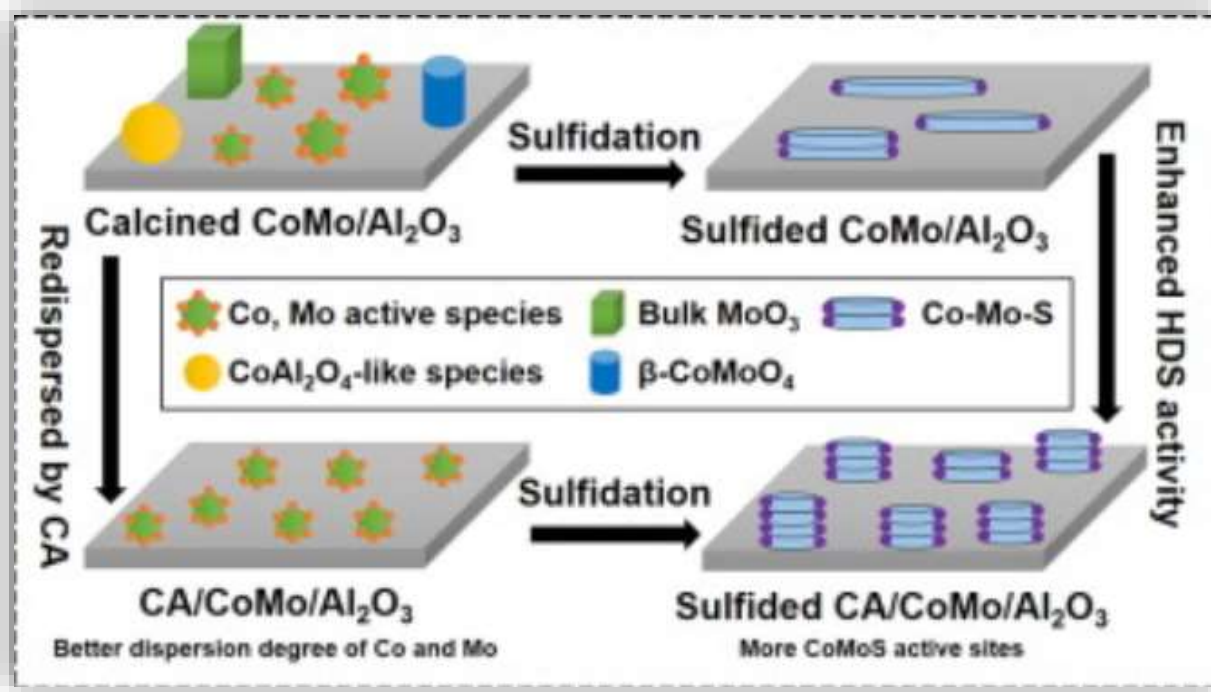
- The catalytic performance of hydrotreating catalysts are closely related to the structure and stability of the active phase.
- The formation of the active phase structure essentially depends on the extents of metal-support interaction.
- The requirements for the extents of metal support interaction decrease in the following order: residue > diesel > gasoline .
- Based on the deep insight into the reaction chemistry, the active phase structure can be designed and constructed by optimizing the parameters of catalysts preparation and sulfidation methods to meet specific demands.

**Table II. Dibenzothiophene (DBT) HDS Activities and MES Phase Composition for Co-Mo/Al<sub>2</sub>O<sub>3</sub> Catalysts Prepared by Different Methods<sup>a</sup>**

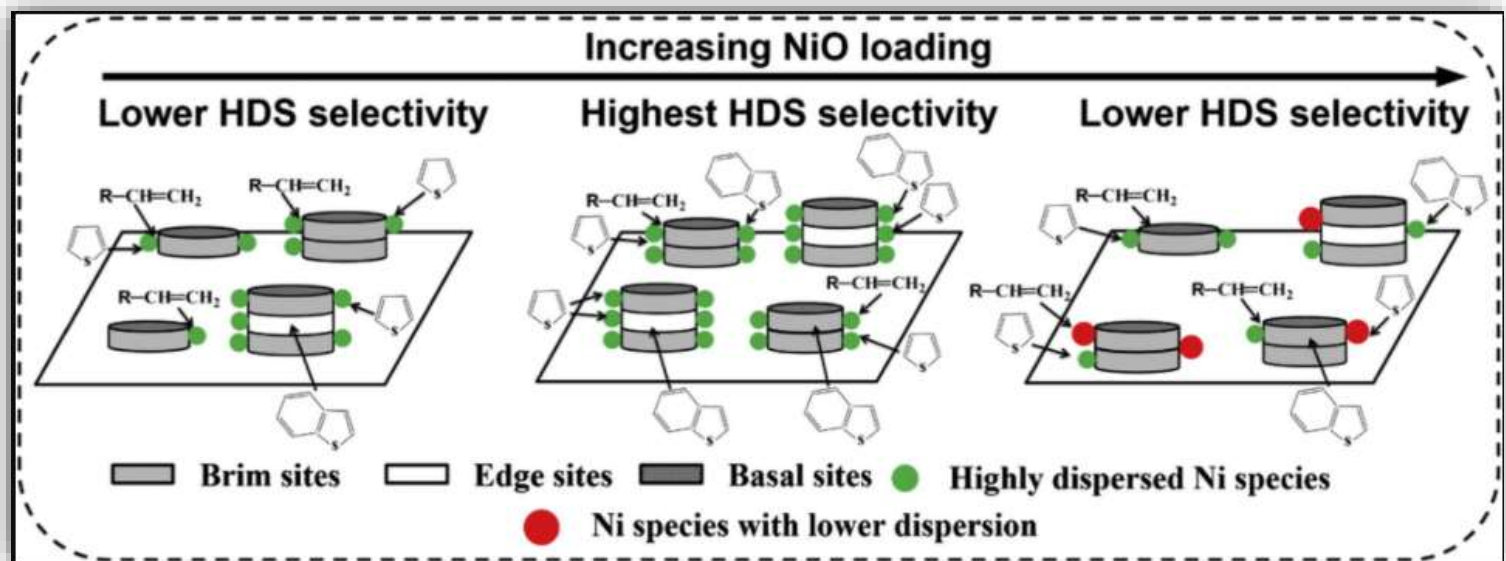
wt % Mo	wt % Co	impregnation method	main phase(s) by MES	DBT conversion, 10 <sup>-8</sup> mol/(s g)
10	3	Mo added first	Co-Mo-S	27
10	3	Co added first	Co-Mo-S	16.3
6	1	Co added first	Co-Mo-S + Co <sub>9</sub> S <sub>8</sub>	12
6	1	equil ads of Mo	Co <sub>9</sub> S <sub>8</sub>	7.3

# Enhanced Activity and Selectivity of HDS





**Enhanced Activity and Selectivity of HDS**



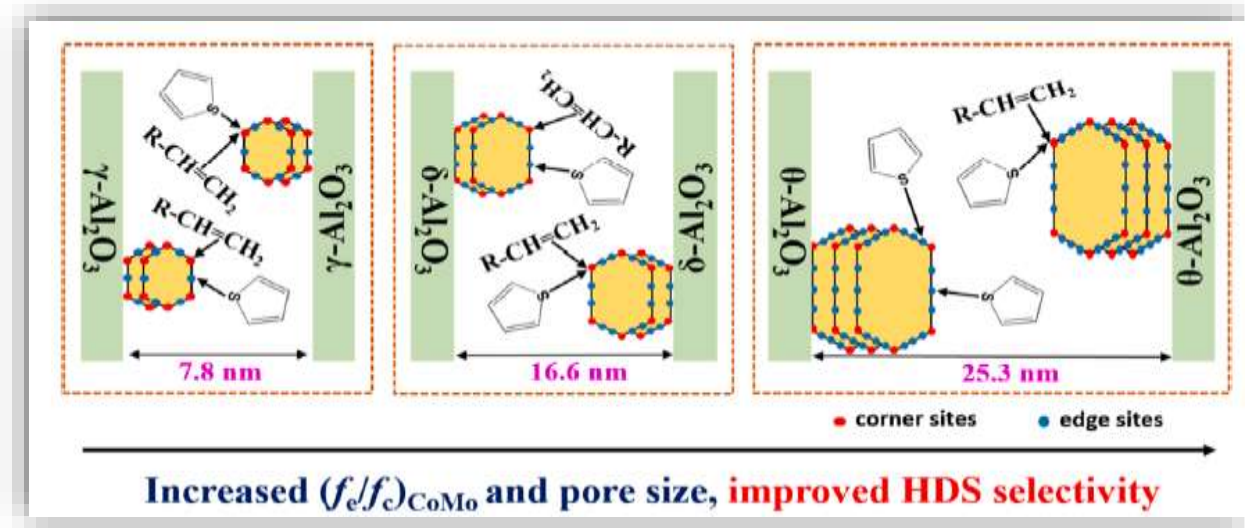
# Effect of the stability of the active phase on catalytic performance

- It is imperative to prepare stable active phase to ensure the desired lifetime of hydrotreating catalysts for diesel and residue.
- The active phase structure undergoes noticeable changes after working at higher temperature and hydrogen pressure for a long period. at higher hydrogen pressure a destacking phenomenon may occur. Such changes in active phase structure may lead to a remarkable decrease in hydrotreating performance and greatly shorten the lifetime of the catalysts.
- For example Co (Ni)-Mo (W)-S active phase may gradually aggregate, and then the promoter Co (Ni) may segregate from the active phase.
- It is vital to decrease the catalyst deactivation by constructing stable active phase structure for ultra-low sulfur diesel production.

**Table III. Comparisons of HDS Activities of MoS<sub>2</sub>, Co<sub>9</sub>S<sub>8</sub>, and Co-Mo-S<sup>f</sup>**

sample	BET surface area, m <sup>2</sup> /g	$k_{\text{HDS}}^a$ , mol/(g of cat. h)	$k_{\text{HDS}}$ , mol/(h mol of surf. atom)
MoS <sub>2</sub>	15.8	$2.9 \times 10^{-4}$	0.9 <sup>b</sup>
Co <sub>9</sub> S <sub>8</sub>	17.8	$4.3 \times 10^{-4}$	1.43 <sup>c</sup>
6.5% Co/Al <sub>2</sub> O <sub>3</sub>		$1.7 \times 10^{-4}$	1.2 <sup>d</sup>
Co-Mo-S <sup>f</sup>		$4.3 \times 10^{-3}$	53 <sup>e</sup>

## Effect of crystal phase of alumina carrier on the selective HDS performance of their corresponding CoMo supported catalysts.

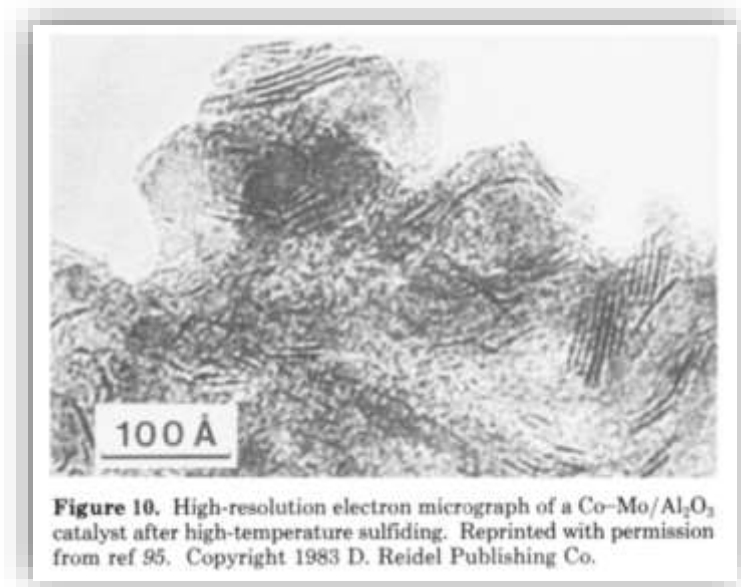


### ***Effect of the structure of the active phase on catalytic performance***

- HDS selectivity correlates linearly with the slab length of (Co)MoS<sub>2</sub> active phase; the longer average (Co)MoS<sub>2</sub> slab length, the better HDS selectivity.
- For example, HDS activity and selectivity of CoMo catalysts correlate linearly with the ratio of Co-Mo-S sites/MoS<sub>2</sub> sites; moreover, larger Co-Mo-S active phase slabs exhibit higher HDS selectivity.

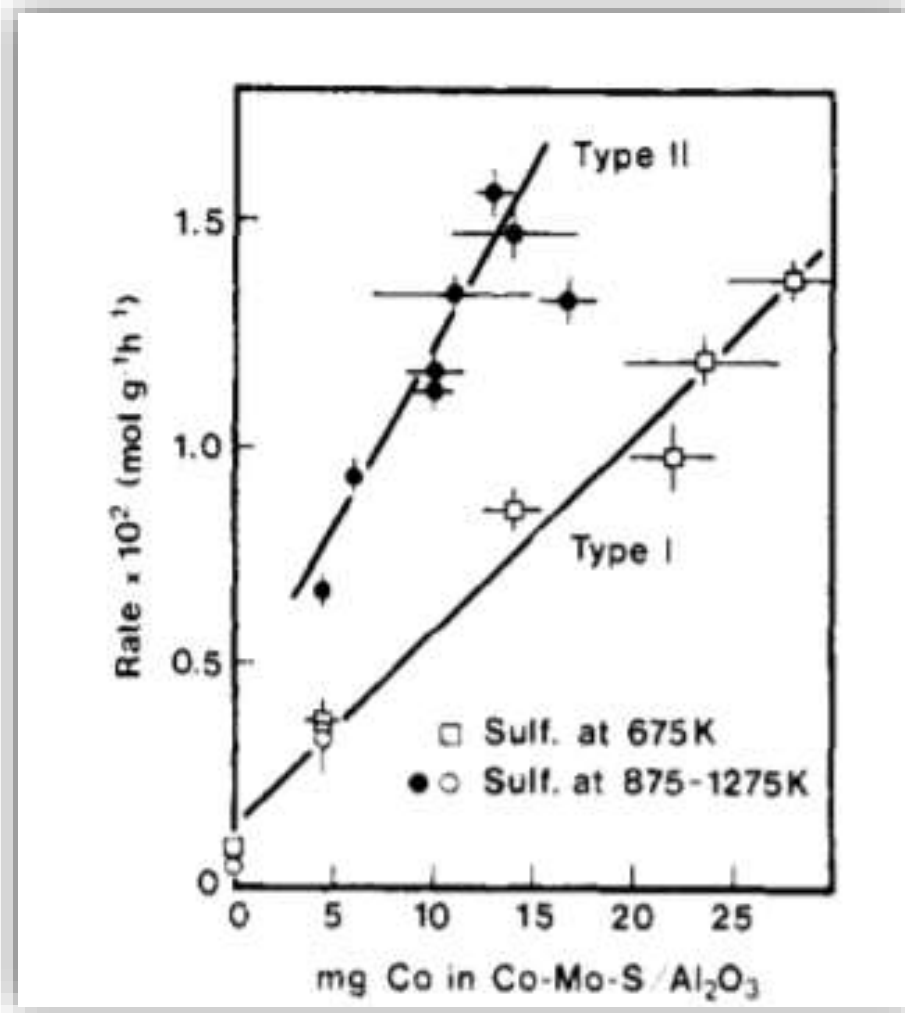
## Effect of sulfidation parameters on the structure of the active phase

- Sulfidation is the key step to transform oxidic state of the catalyst to sulfided state and form the active phase structure. The parameters of sulfidation, including the state of the reaction medium (gaseous or liquid) and sulfiding agents, pressure, temperature and gas composition have great influence on the formation of active phase structure.
- It indicated that in contrast to  $\text{H}_2\text{S}/\text{H}_2$ , the sulfidation gas in the absence of  $\text{H}_2$  (e.g.  $\text{H}_2\text{S}/\text{N}_2$  or  $\text{H}_2\text{S}/\text{He}$ ) can greatly promote the sulfidation of supported metal species and weaken the interaction between the active phase and support, but the morphology of the active phase may vary with the types of support and preparation methods.
- Thus we can say that Active phase can be designed by adjusting preparing and sulfiding parameters.



# **Effects of the Active Phase of CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts Modified Using Cerium and Phosphorus on the HDS Performance for FCC Gasoline**

- Hydrodesulfurization (HDS) of gasoline is the most widely applied and effective technology at present. Traditionally, HDS catalysts used alumina as a support and Co- or Ni-modified MoS<sub>2</sub> crystallites as the active phase.
- But traditionally HDS catalysts exhibit high hydrogenation of olefins activity, causing serious loss of the gasoline octane number. In order to overcome this problem and improve the performance of HDS catalysts, it is imperative to develop a catalyst with high HDS/HYDO selectivity to maximize desulfurization and minimize olefin hydrogenation (HYDO).
- The morphology of HDS catalyst active phase directly determines the catalytic properties.
- The active phase of HDS catalysts has two types: “Co–Mo–S-I” and “Co–Mo–S-II”. The “Co–Mo–S-I” active phase appears as a single layer distribution, and the metal–support interaction (MSI) is stronger. The “Co–Mo–S-II” active phase presents a multilayered stacking state with weaker MSI and a higher sulfidation degree.



HDS activity as a function of the amount of Co in Co-Mo-S for catalysts sulfided at different temperatures.



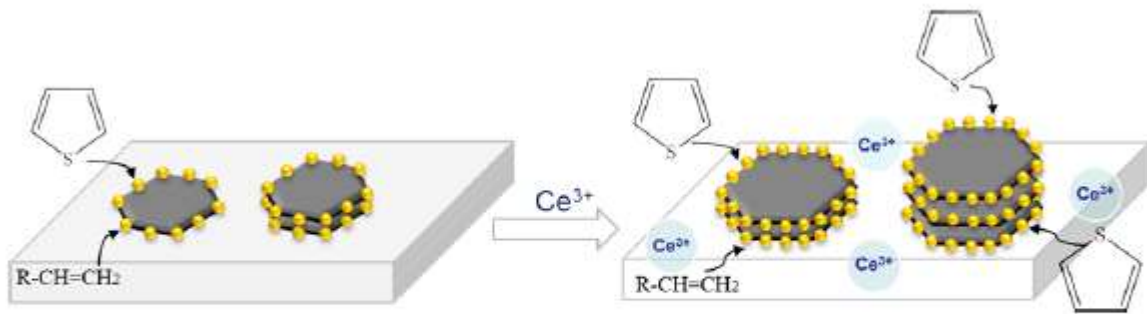
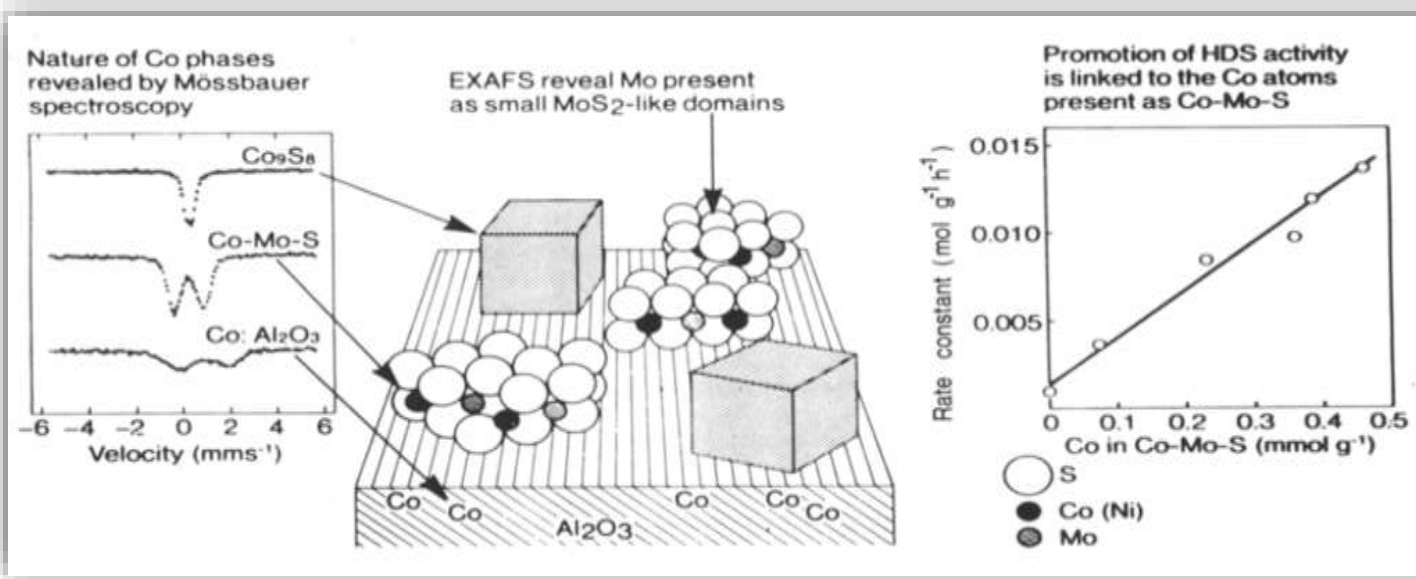
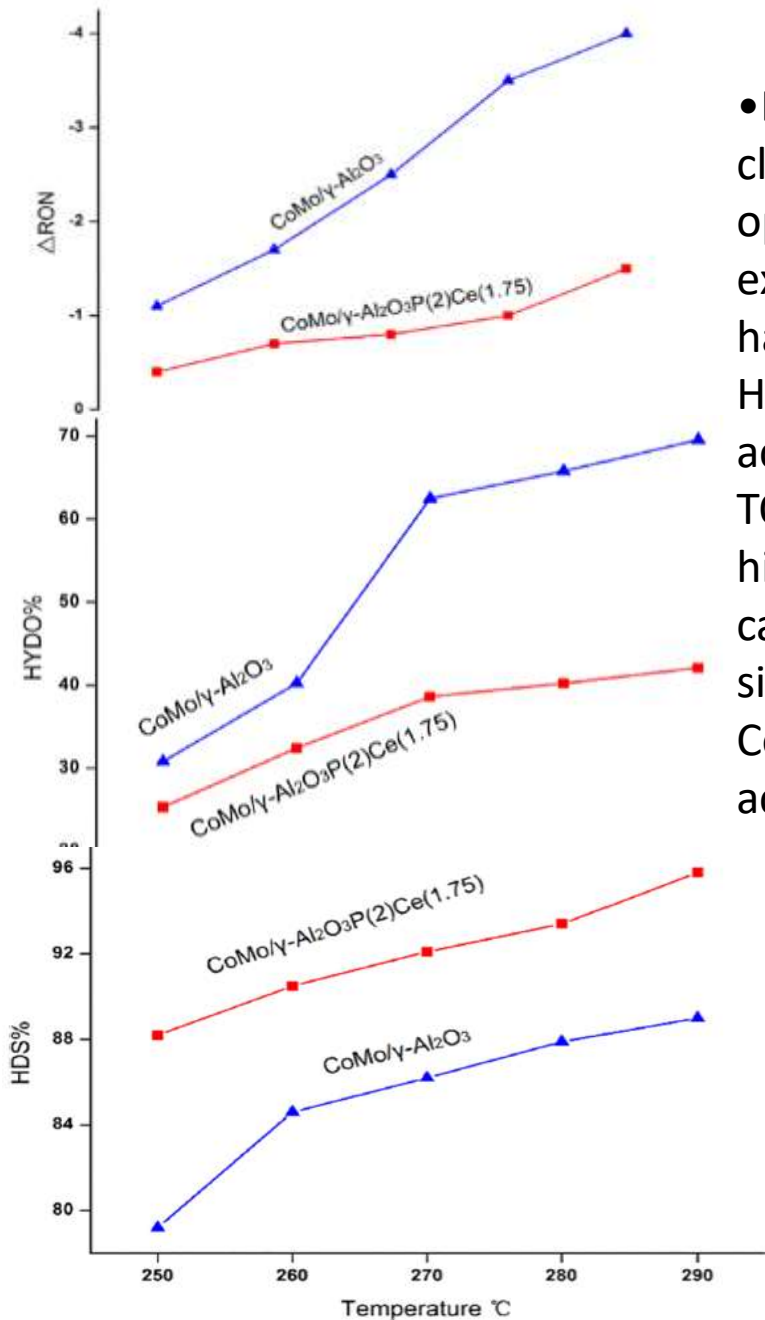


Figure 9. Schematic illustration of cerium influence on the active-phase morphology.

The morphology of the active phase of sulfide catalysts generally exhibited by HRTEM and XPS methods.



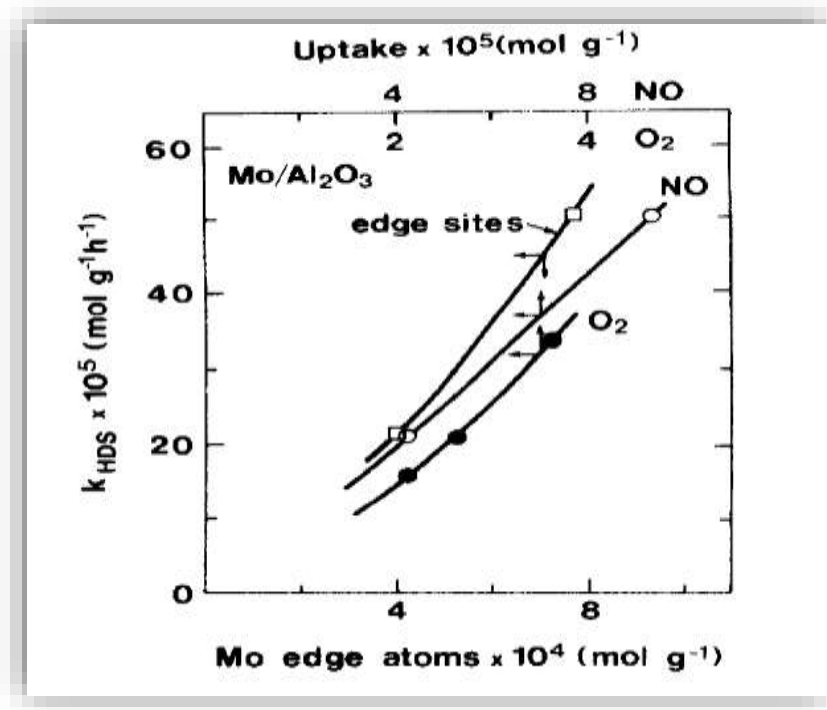
**Typical Co-Mo/Al<sub>2</sub>O<sub>3</sub> HDS catalyst**



• By comparing XPS and HRTEM data, it can be clearly seen that the addition of cerium can optimize the morphology of the active phase. The experimental results support the hypothesis that Ce has the ability to promote HDS activity and inhibit HYDO reaction by modifying the morphology of the active phase. As shown in Figure, the values of TOFHDS for CoMo/γ-Al<sub>2</sub>O<sub>3</sub>P(2)Ce(1.75) catalyst is higher than those for the CoMo/γ-Al<sub>2</sub>O<sub>3</sub>Ce(1.75) catalyst, suggesting that using Ce and P simultaneously as modifiers can optimize the CoMoS active phase and further promote the HDS activity.

Dependence of HDS, HYDO and ΔRON of FCC gasoline hydrotreatment on temperature over CoMo/γ-Al<sub>2</sub>O<sub>3</sub> and CoMo/γ-Al<sub>2</sub>O<sub>3</sub>P(2)Ce(1.75) catalysts.

The HDS reaction may not necessarily involve all edge sites. For example, it is likely that the MoS<sub>2</sub> edges will contain both different geometric configurations Of the MO atoms (e.g., corner and edge sites) and sulfur vacancies (monovacancies, di-vacancies, vacancy pairs, etc.).



Dependance of the thiophene HDS activity of Mo/Al<sub>2</sub>O<sub>3</sub> catalysts on MoS<sub>2</sub> edge sites, O<sub>2</sub> uptake and NO uptake. O<sub>2</sub> uptakes on catalysts sulfided at 873 K; NO uptakes on catalysts sulfided at 673 K; concentration of MoS<sub>2</sub> edge sites has been determined by means of EXAFS on catalysts sulfided at 673 K.

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Influence of the alumina crystal phase on the performance of CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts for the selective hydrodesulfurization of fluid catalytic cracking naphtha *Fuel* 289 (2021) 119843