

Development of high-performance diesel hydrotreating catalyst: Concepts to commercial success

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Abstract

A new Ni-Mo based catalyst composition, INDICAT-DH-IV, was developed and manufactured by a proprietary catalyst preparation technology for diesel hydrotreating. The catalyst has been performing in commercial scale since June 2009, consistently producing ultra low-sulfur diesel of Euro-IV/V standards from a feedstock containing 1.75 wt% sulfur. In addition to lowering of sulfur, the catalyst also enhances cetane number and reduces boiling end point to obtain diesel with better quality. The catalyst was characterized by X-ray photoelectron spectroscopy to ascertain the electronic state of metal species. The morphological characterization of the catalyst carried out by TEM revealed the presence of nano-sized MoS₂ slab structures. The performance of the catalyst is mainly attributed MoS₂ slabs with increased stacking which in turn are generated from the customized metal-sulfide precursors.

Key words: nickel-molybdenum; XPS; TEM; commercialization of catalyst; hydrodesulfurization; diesel hydrotreating; centane index; VGO desulfurization

1. Introduction

Hydrotreating technology has evolved considerably in the last two decades to meet the regulations enforced worldwide on fuel quality particularly with regard to the sulfur content. Following the global trend on the diesel specifications, the use of BS-IV diesel with < 50 ppmw sulfur (equivalent to EURO-IV) had already begun in various metro cities in India. Consequently, refiners are challenged to produce ultra low-sulfur diesel (ULSD) with minimal capital investment. However, since the existing hydrotreaters are designed only for low severity operation, these units cannot be operated at elevated conditions for enabling deep desulfurization. To overcome this difficulty, a high active catalyst system can be employed in the existing units as a cost-effective option for ULSD production [1-4].

In order to address the demand for high-performance hydrotreating catalysts, the development of new catalyst versions suitable for commercial exploitation was undertaken. The catalyst formulation optimized at laboratory scale was suitable for the

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desulfurization of diesel to the level of 10-50 ppmw at appropriate operating conditions. The commercial feasibility of this formulation has been successfully established by manufacturing in bulk scale and using it under commercial plant conditions since June 2009. The present paper describes the commercial performance and also some prominent features of INDICAT-DH-IV catalyst.

2. Experimental

2.1. Catalyst preparation and characterization

The Ni-Mo/Al₂O₃ based catalyst system was prepared as 1.2 mm trilobe extrusions using a proprietary preparation technology in which specially designed metal precursors were incorporated in an alumina support with appropriate porous texture [5]. X-ray photoelectron spectra (XPS) of the newly designed catalyst system were recorded using a VG Scientific ESCA Lab MK-II photoelectron spectrometer. The catalyst samples were also characterized for surface morphology using Jeol-JEM-2100 electron microscope with LaB₆ filament as a source of electrons.

The catalyst sample was sulfided in a stream of 10% H₂S/H₂ (100 ml/min) at 350 °C for 4 hours prior to the characterization by XPS and TEM. For activity evaluation, sulfidation of catalyst was carried out in liquid phase at 330 °C and 30 bar using gas oil spiked with 5% of Dimethyl disulfide as feedstock.

2.2. Performance evaluation & commercial demonstration

The catalytic activity was evaluated in laboratory scale (5-20 ml catalyst) using a high pressure, isothermal fixed bed micro reactors operating in a down flow mode. The commercial demonstration run was carried out in a hydrotreating unit of a refinery. The details of laboratory test and demonstration run are given in Table 1.

Table 1
Catalyst performance test & demonstration conditions

Parameters	Conditions	
	Laboratory test	Commercial demonstration
Feed sulfur (w%)	1.80	1.75
H ₂ pressure (Bar)	49	55
H ₂ /Oil ratio (Nm ³ /m ³)	250	330
LHSV (h ⁻¹)	1.5	0.72
Temperature (°C)	325-350	355-370

2.3. Product Analysis

The total S and N content in the feed and product samples were analyzed based on oxidative pyro-fluorescence and pyro-chemiluminescence using an ANTEK 7000 Total Sulfur & Nitrogen analyzer.

3. Results and Discussion

3.1. Design of high-active catalyst

Various factors have been considered for the design of the high active catalyst [6-14]. The alumina support used was carefully optimized to obtain enhanced diffusivity in the catalyst. The major strategies adopted were optimization of metal-support interactions and fine-tuning of metal sulfide precursors for generating of high-active reaction sites. Based on these design philosophy, a high-active hydrodesulfurization catalyst was developed. The typical properties of the catalyst are given in Table 2.

Table 2.
Properties of the INDICAT-DH-IV catalyst

Active metals	Ni & Mo
Metal contents (w%)	NiO:3-4; MoO ₃ : 15-17
Support	γ -alumina
Surface area (m ² /g)	> 200
Extrudate shape	Trilobe
Diameter (mm)	1.2
Average length (mm)	4-6
Side crushing strength (Kg/mm)	> 1.0

3.2. X-ray photoelectron spectroscopy (XPS) studies

X-ray photoelectron spectra of the fresh and sulfided catalysts were recorded to elucidate the electronic state of molybdenum and nickel sites on the catalyst surface. The Mo 3d spectra for the fresh and sulfided catalysts are shown in Fig. 1. Table 3 provides the binding energy and full widths at half maximum (FWHM) obtained from Mo 3d and Ni 2p_{3/2} spectra of the catalysts. The Mo 3d binding energy of pure MoO₃ crystallites is reported to be 233.5 eV, whereas lower binding energies of 232.70 and 228.44 eV are observed for fresh and sulfided NiMo catalysts, respectively. The lowering of binding energies might be due to the changes of average valence state of molybdenum species, resultant of the interactions of Mo species with the support surface [15, 16]. Metal sites in higher oxidation states are believed to experience higher binding energies. Thus, the lowering of binding energy on sulfidation could be attributed to the conversion of Mo species in higher oxidation states to Mo^{IV} S₂ phases.

FWHM of both Mo 3d and Ni 2p_{3/2} bands is found to be higher for the fresh catalyst as compared to the sulfided catalysts. In the case of fresh catalyst, the broadening of the bands might be caused by the strong interactions between the metal sites and support [16-17]. The lowering of peak broadening for sulfided catalyst indicates the existence of NiMoS phases as layered slabs, which experience only weaker interactions with the support [15-17]. The formation of NiMoS slabs is corroborated by TEM micrographs of the sulfided catalyst.

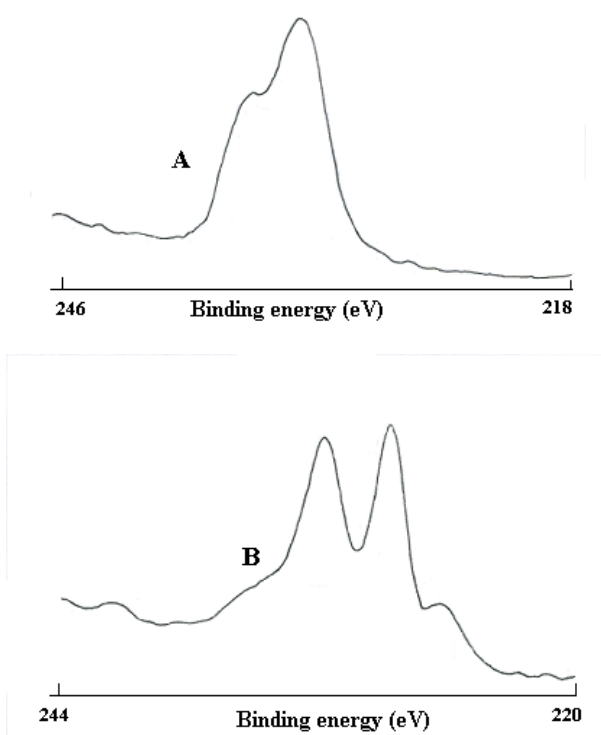


Fig. 1: XPS Mo 3d spectra of (A) fresh and (B) sulfided INDICAT-DH-IV catalyst

Table 3
XPS data of fresh and sulfided INDICAT-DH-IV catalyst

Catalyst	Mo 3d		Ni 2p _{3/2}	
	Binding energy (eV)	FWHM (eV)	Binding energy (eV)	FWHM (eV)
INDICAT-DH-IV (Fresh)	232.70	5.648	854.70	4.336
INDICAT-DH-IV (Sulfided)	228.44	2.124	853.64	3.084

3.3. Transmission electron microscopy (TEM) studies

Hydrotreating reactions take place at the edges of hexagonal MoS₂ slab structures, which can be easily visualized by transmission electron microscopy (TEM). The morphology of the newly developed catalyst was characterized using TEM and the morphological parameters are calculated from the micrographs as described elsewhere [18-20]. Typical micrograph of the catalyst showing the slab structure of MoS₂ phases is shown in Fig.2. The morphological parameters like number of slabs, stacking degree, Mo dispersion and corner & edge Mo atoms are given in Table 4. The morphological parameters observed for the newly developed catalyst are in the same range of that reported for similar high active catalysts [21-22]. The individual slab structures in a typical micrograph, which are more than 100 in number, are carefully studied and the distribution of slabs with respect to the degree of stacking is plotted as in Fig. 3.

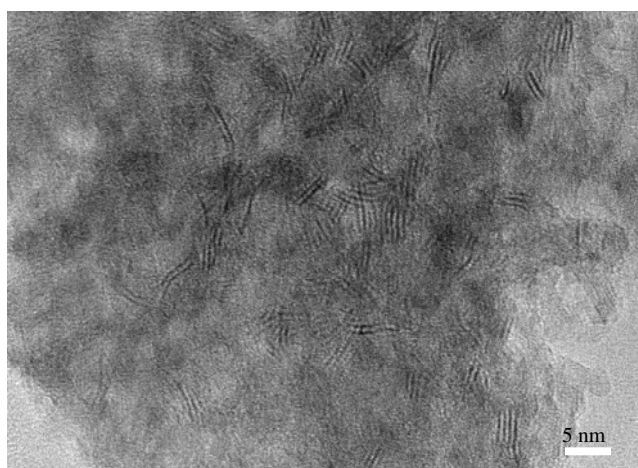


Fig. 2: Typical TEM of INDICAT-DH-IV catalyst

Table 4
Morphological parameters of INDICAT-DH-IV catalyst

Morphological parameter	Value
Average layer length (Å)	44
MoS ₂ slab distance (Å)	6.1
Average stacking degree	3.99
Mo dispersion	0.3
% of Mo atoms in the corner	5
% of Mo atoms in the edge	25

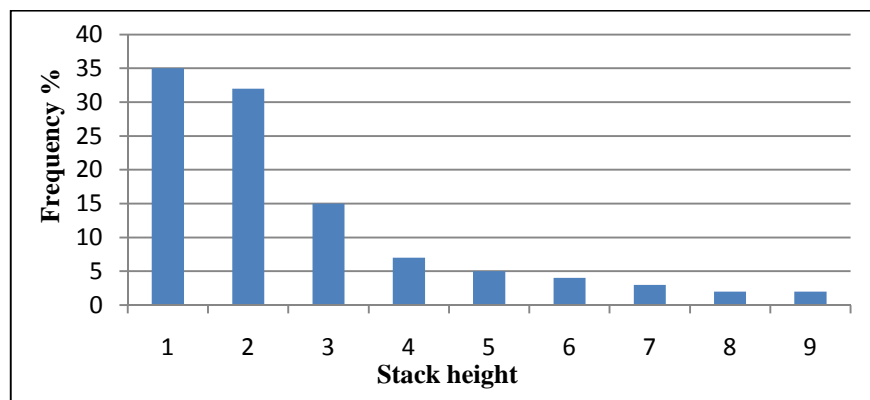


Fig. 3: Distribution of MoS₂ slabs with respect to stack height

TEM data of INDICAT-DH-IV is compared with that of low-active catalysts prepared by conventional catalyst preparation methods. The ratio of frequency of multilayer to monolayer slabs is found to be in the range 1.5-2.0 for INDICAT-DH-IV catalyst samples whereas in the case of conventional lab generated low-active catalyst systems, the values are only in the range 0.4-0.8. The formation of multilayer slabs in large numbers accounts for the high performance of the new catalyst [22-23].

Hydrotreating catalysts are known to be unstable during the initial stages of the reaction. The catalyst activity is likely to be deteriorated very sharply due to deactivation by possible sintering of the active phases and the deposition of coke on the catalyst surface and subsequently a steady state activity is exhibited after initial stabilization [24]. In order to study the changes in catalyst morphology during the start-up, spent catalyst after 5 days on stream was also characterized. The ratio of frequency of multilayer to monolayer slabs of the spent catalyst was found to be almost same as that of the fresh sulfided catalyst. This observation indicates that the newly designed catalyst formulation is robust and tolerant to initial deactivation of the active phases which are quite likely for similar systems.

3.4. Catalyst performance in laboratory and commercial scale

The performance data of the catalyst obtained from the laboratory scale evaluations are given in Table 5. The superior performance prompted scale-up of the new recipe to commercial levels. Further, the performance demonstration of the catalyst for producing EURO-IV grade diesel is being carried out commercially since June 2009.

Table 5
Catalyst performance data in laboratory scale

Catalyst	Pressure (Bar)	LHSV (h ⁻¹)	Temp. (°C)	* Relative volume activity (RVA)
Conventional catalyst	49	1.5	335	100
Reference catalyst	49	1.5	325	87
	49	1.5	335	180
	49	1.5	345	420
INDICAT-DH-IV catalyst	49	1.5	325	100
	49	1.5	335	180
	49	1.5	345	410

* RVA= $k_{\text{HDS}}(\text{INDICAT or Reference}) \times 100 / k_{\text{HDS}}(\text{Conventional})$
 k_{HDS} = Rate constant of hydrodesulfurization reaction

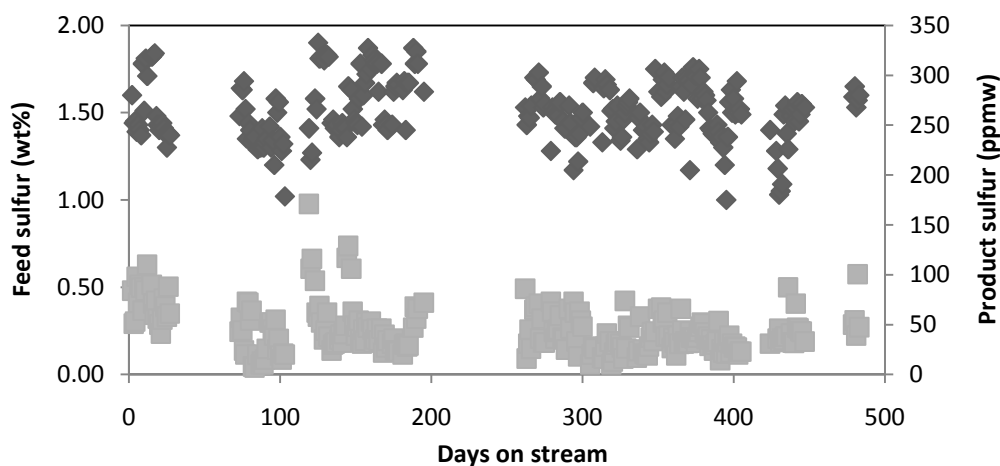


Fig. 4: Commercial performance of INDICAT-DH-IV catalyst in diesel mode

The sulfur content in the diesel feed and products during 350 days on stream is plotted in Fig.4. The catalyst has consistently exhibited high-performance and produced diesel with an average sulfur content of 44 ppmw from feed with about 1.75% sulfur. Cetane improvement by 6-7 units was also observed in the diesel product even at moderate operating conditions of 55 bar. Catalyst was also used for the desulfurization of VGO and was able to desulfurize VGO to the level of about 80% during the 50 days on stream as depicted in Fig. 5. It is also evident from Fig 5 and 6 that the catalyst has shown sustained

performance without any major deterioration of activity during the period on stream. The performance data indicate that the developed catalyst is capable for hydrotreating of gas oil feeds under commercial hydrotreating process conditions to produce diesel meeting BS-IV standards.

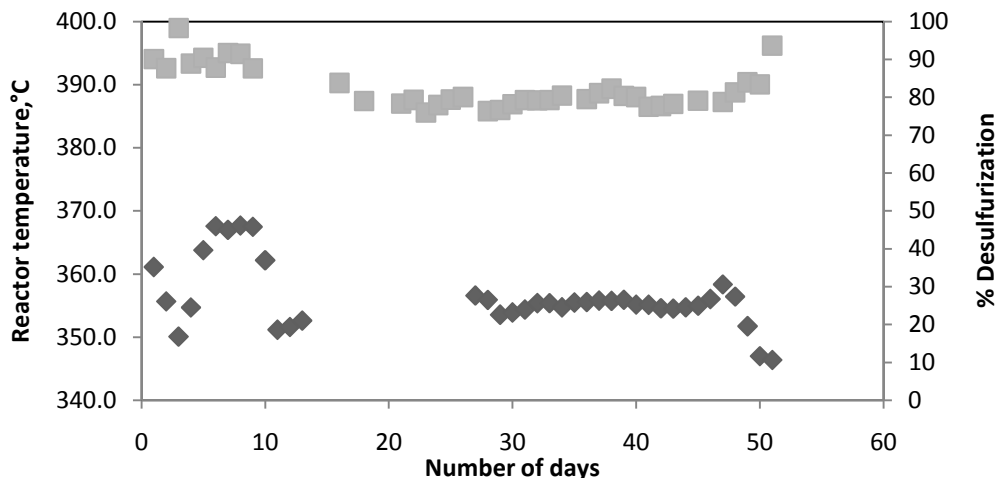


Fig. 5: Commercial performance of INDICAT-DH-IV catalyst in VGO mode

4. Conclusions

The refining industry is dependent on the development of high-active catalysts for the desulfurization of diesel fuel to meet the regulations imposed by legislative authorities. The knowledge on the reactivity and reaction pathways of various refractory sulfur compounds has stimulated the development of a novel NiMo/Al₂O₃ based catalyst. The fundamental understanding on the effect of support interactions, role of metal precursors and catalyst morphology and their interrelation with catalyst activity has led to the evolution of this high-active catalyst. The promising commercial performance of the newly formulated catalyst recipe is expected to provide new opportunities for wide commercial application.

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