

Comparative Study of New Re-Ni-Mo/Al₂O₃ and Conventional Hydrodesulphurization Catalyst

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Abstract

New types of hydrodesulfurization (HDS) catalyst Re-Ni-Mo/ γ -Al₂O₃ was prepared and tested separately with two prepared conventional HDS catalysts (Ni-Mo/ γ -Al₂O₃ and Co-Mo/ γ -Al₂O₃) by using a pilot plant hydrotreatment unit. Activities of three prepared hydrodesulfurization catalysts were examined in hydrodesulfurization (HDS) of atmospheric gas oil at different temperatures 275 to 350 °C and LHSV 1 to 4 h⁻¹, the reactions conducted under constant pressure 40 bar and H₂/HC ratio 500 ml/ml. Moreover, the hydrogenation of aromatic (HAD) in gas oil has been studied. HDS was much improved by adding promoter Re to the Ni-Mo/Al₂O₃ catalyst. The results showed that Re-Ni-Mo/ γ -Al₂O₃ have more activity in desulfurization than Ni-Mo/ γ -Al₂O₃ and Co-Mo/ γ -Al₂O₃ catalysts. The efficiency of hydrodesulfurization was markedly reduced over the Co -Mo/ γ -Al₂O₃. Also the result showed that Ni-Mo/ γ -Al₂O₃ have a minimum aromatic content 15.44 %.

Key Words: Hydrodesulfurization, Hydrogenation of aromatic, HDS catalyst, Physical Adsorption

Introduction

Sulfur removal from petroleum derivatives is a very important industrial process. Diesel fuel and gasoline must have much lower heteroatom content, and this is done by Hydrotreating process. The main aim of hydrotreating is to diminish air pollution emissions, to avoid poisoning of noble metals and to improve the fuel quality. Catalysts are used in a variety of applications from the production of consumer goods to the protection of the environment [1]. The reduction of diesel engine emissions is a rather complex issue with a number of

possible solutions. One of these solutions is the improvement of diesel fuel quality, especially by lowering the sulfur and aromatics content and increasing the cetane number. Lower levels of aromatics will help to maximize the regeneration cycle of the exhaust gas treatment devices in addition to the reduction of PM emissions. The two-stage hydrotreating has the flexibility to cope with the simultaneous reduction in sulfur and in aromatics [2]. Extreme reductions in the sulfur content will have an enormous impact on the costs and technology for diesel fuel production.

Optimum design and efficient utilization of catalysts require a thorough understanding of the surface structure and surface chemistry of the active material. Utilization of more active catalysts for hydrodesulfurization (HDS) of liquid fuel would be the less costly and the most effective way for the refineries, because it would allow for avoiding modifications of plant installations [3]. Usually the HDS catalysts contain molybdenum sulfide promoted with cobalt or nickel and supported on a high surface area alumina, but it is difficult to prepare a kind of catalysts with high active metals content because of the limitation of support's porous structure. Currently, new catalysts appear for HDS reactions, which contain active components.

HDS catalysts possess high catalytic activity, but they have the disadvantage of high cost. Many investigations of the hydrotreatment of petroleum based feedstocks show that the current commercial catalysts based on molybdenum sulfide doped with Ni or Co do not have sufficient activity to meet today's refinery requirements determined by the environmental standards [4]. To attain compliance in the future, new hydrotreatment catalysts are necessary for the hydrodesulfurization (HDS) of feedstocks.

To improve the performance of the HDS catalyst, all steps in the preparation procedure should be considered. The key parameters are the choice of a precursor of the active species, support, promoter, synthesis and post-treatment of the synthesized catalyst [5].

In the last two decades, other transition metal sulfides have been investigated. The application of noble metal catalysts for deep HDS is limited by their sulfur resistance.

Therefore, those catalysts are normally used when most of the sulfur compounds and H₂S have been removed from the process stream. A new concept of bifunctional catalysts has been proposed to increase the sulfur resistance of noble metal hydrotreating catalysts. It combines catalysts supports with bimodal pore size distribution (e.g. zeolites) and two types of active sites. The first type of sites, placed in large pores, is accessible for organosulfur compounds and is sensitive to sulfur inhibition. The second type of active sites, placed in small pores, is not accessible for large S-containing molecules and is resistant to poisoning by H₂S [6]. Since hydrogen can easily access the sites located in small pores, it can be adsorbed dissociatively and transported within the pore system to regenerate the poisoned metal sites in the large pores.

However, the need of catalysts having better hydrogenation properties would increase in the future, due to the necessity for hydroprocessing of the heavy oil fractions of petroleum and even deeper HDS reactions [7]. Since the Re sulfide has higher hydrogenation activity than the Mo or W sulfides [8], this capability of the Re sulfide can greatly help in the development of a new generation of better hydrotreating catalysts, especially when the reaction mechanism requires or is predominantly through a prehydrogenation route, as it occurs in deep HDS and HDN reactions. The objective of this study is an attempt to provide a new HDS catalyst Re-Ni-Mo/ γ -Al₂O₃ and compared the efficiency and activity with traditional catalysts.

Experimental Work

Feedstock

Iraqi atmospheric gas oil (supplied by Al-Dura Refinery -Baghdad) is used as a feedstock in the present investigation. Table 1 shows the specifications of Iraqi Gas Oil.

Table 1, Properties of atmospheric gas oil

Specification	Value
Specific gravity at 15.6 °C/15.6 °C	0.8289
API gravity	37.6
Viscosity / 40 °C, C.st	6.62
Sulfur content, wt. %	1.402
Aromatic content, wt. %	18.66
Flash point, °C	82
Pour point, °C	-9
Diesel index	63
Aniline point, °C	71.5
Cetane Number	57
Colour, ASTM	0.5

Materials

1- Support

Alumina support (γ - Al_2O_3) with spherical shape and an average diameter of 3mm was supplied by the FLUKA AG Company. The properties of γ - Al_2O_3 are tabulated in Table 2.

Table 2 Properties of γ - Al_2O_3

Surface Area, m^2/g	280
Pore Volume, cm^3/g	0.365
Porosity	0.45
Bulk density, g/cm^3	1.06
Crushing strength, Kg	18
Loss in attrition, wt. %	1.6

2- Gases

Nitrogen

Nitrogen was supplied from Baghdad Company with purity 99.9 %.

Hydrogen

Hydrogen was supplied from Baghdad Company with purity 99.9 %.

Catalyst Preparation

1- Impregnation Apparatus

The impregnation apparatus consists of a conical flask conducted with a separating funnel, vacuum pump, electric shaker and trip to absorb the moisture and gases for efficient deposition of metals oxides into the carrier, the flask fixed upon shaker to ensure good contacting between aqueous solution and alumina particles. The objective is impregnation of carrier with aqueous solution of metal salt which adjusted to concentration which gives desired metal loading.

2- Preparation of Co-Mo/ γ - Al_2O_3 Catalyst

The Co-Mo/ γ - Al_2O_3 Catalyst was prepared by evacuation 100 g of γ - Al_2O_3 to remove the adsorbed gases and moisture, then this alumina calcined in oven at 538 °C for 16 hours. The catalyst was prepared by impregnation method [9]. An impregnation aqueous solution was prepared by dissolving 11 g of cobalt carbonate, 4 g of phosphoric acid [$\text{H}_3(\text{PMo}_{12}\text{O}_{40})\cdot 30\text{H}_2\text{O}$], and 38 g of phosphomolybdic acid in 75 cm^3 of water with shaking then this solution was poured in the conical flask of the impregnation apparatus containing 100 g of dried gamma alumina. The impregnation took place in an impregnation apparatus for 3 hours. The impregnated carrier was air dried at 120 °C for 16 hours and then calcined at 538 °C for 16 hours.

3- Preparation of Ni-Mo/ γ -Al₂O₃ Catalyst

The Ni-Mo/ γ -Al₂O₃ catalyst was prepared at the same apparatus, conditions and quantities mentioned above except for cobalt carbonate which was substituted by nickel carbonate.

4- Preparation of Re-Ni-Mo / γ -Al₂O₃ Catalyst

Re-Ni-Mo / γ -Al₂O₃ catalyst was prepared by multistage technique. Thus, the first step, Ni-Mo/ γ -Al₂O₃ was prepared as mentioned above. In the second stage 22.78 g of Ni-Mo / γ -Al₂O₃ was impregnated with 25 cm³ of an aqueous solution having 0.96 g NH₄ReO₄ per liter solution.

The impregnated material was air dried at 120 °C for 16 hours and calcined at 538 °C for 16 hours [10].

Catalytic Activity Test

Catalytic activity studies were carried out in a continuous hydrotreating pilot plant unit. The hydrotreating unit designed by (VINCI technologies). The unit (shown in fig. 1) consists mainly of vertical tubular stainless steel reactor (17.5 mm I.D., 25.5 mm O.D. and 300 mm length) electrically heated in a two block oven, temperature controller, dosing pump, gas meter and high pressure separator. Hydrogen gas was supplied to the unit from a hydrogen cylinder.

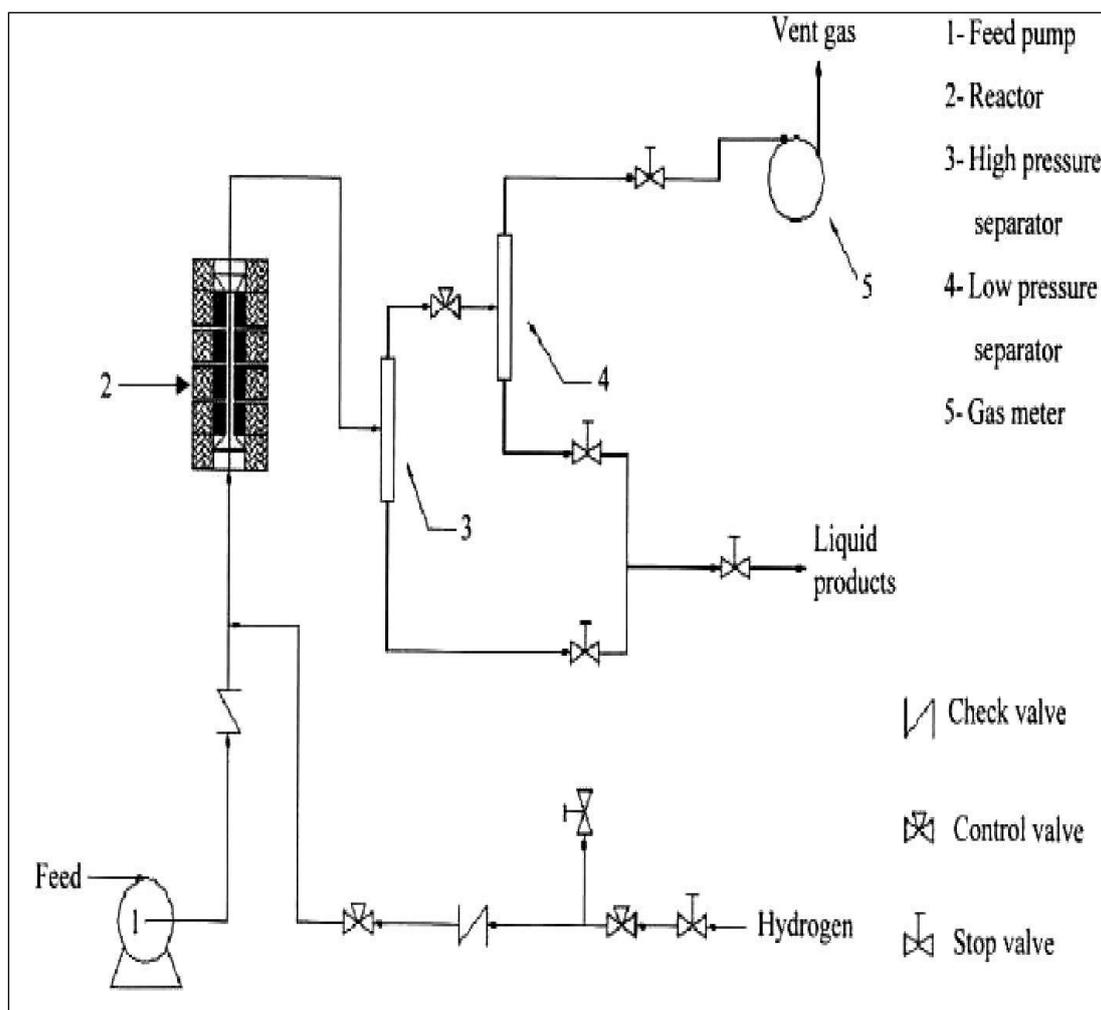


Fig 1 Schematic diagram of the hydrodesulfurization unit

50 g of catalyst (catalyst layer length 23 cm) was loaded into the mid-section of the reactor, while the upper and lower sections were packed with ceramic balls (ceramic layer length 3.5 cm). The unit was purged with nitrogen to ensure oxygen removal from the system, the pressure increased gradually up to 65 bars for 3h to check leaks, then pressure reduced to 10 bar and change nitrogen by hydrogen with 99.99% purity. The static hydrogen pressure increased up to 65 bars to check the leaks again. The hydrogen pressure reduced to 5 bars to prepare the unit for sulfiding process.

Pre-sulfiding was carried out at pressure 30 bars, temperature 310°C, and feed flow rate 1ml/min for 12h using gas oil with 1.402 wt. % sulfur content.

The hydrotreating of gas oil was carried out at 40 bar hydrogen pressure, 1 to 4 h⁻¹ LHSV, 275 to 350 °C reaction temperatures and hydrogen to hydrocarbon ratio 500 l/l. The liquid product was collected (after a stabilization period to attain a steady state, this time depends on operating conditions of sample) in a receiver from which samples were taken for analysis.

Results and Discussion

1- Surface area and Pore volume

The specific surface area determination was carried out using the BET isotherm, nitrogen adsorption and desorption isotherms were measured on Thermo Finnegan type instrument. The specific surface area [S_A] which is the area in m² of one gram of solid is calculated as in equation.

$$S_A = \frac{Vm}{22400} \times a_m \times N \times 10^{-20} \dots (1)$$

Where V_m is the monolayer coverage, a_m is the area occupied by

one molecule of adsorbate in the monolayer which is 0.162 nm² for nitrogen molecule, and N is Avogadro's constant, 6.02×10^{23} molecules / mol.

Results of surface area and pore volume are tabulated in Table 3.

Table 3, surface area and pore volume of prepared catalysts

	Co-Mo/ γ -Al ₂ O ₃	Ni-Mo/ γ -Al ₂ O ₃	Re-Ni-Mo/ γ -Al ₂ O ₃
surface area, m ² /g	178.5	191.4	235.23
pore volume, cm ³ /g	0.34	0.38	0.38

The results of surface area and pore volume values for three prepared catalysts show that maximum surface area has for Re-Ni-Mo/ γ -Al₂O₃, this is due to the high quantity of mesoporous of prepared catalysts [11]. Furthermore, a large specific surface area is preferable to providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces, high surface area usually has a high percentage of small pores, in general the use of Re leads to the development of a porous system. Co-Mo/ γ -Al₂O₃ catalyst shows a minimum surface area and this may be due to blockage some pores in preparation steps [12], and this mean that a reduction in pore sites is occur and this lead to a reduction in the activity of catalyst. Pores that are larger than necessary, lend little to improving diffusion characteristics and as the pore diameters of the catalyst increase the surface area decreases (at constant pore volume). Activity, generally, decreases with decreasing of the surface area and loss in pore volume occurs in the smallest diameter pores first.

Highest activity retention is maintained if pore volume is concentrated in a very narrow range of pore diameters.

2- Pore Size Distribution

Figures 2, 3 and 4 show the pore size distribution for three prepared catalysts. The Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ catalysts showed a number of pores toward macro size diameter, while Re-Ni-Mo/ γ -Al₂O₃ catalysts exhibit only meso-pores after active metal impregnation. This is certainly effect on pore-size distribution change with a decrease in total pore volume.

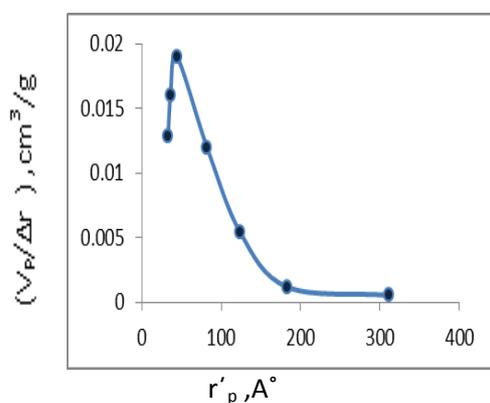


Fig.2, Pore size distribution of prepared Co-Mo/ γ -Al₂O₃ catalyst

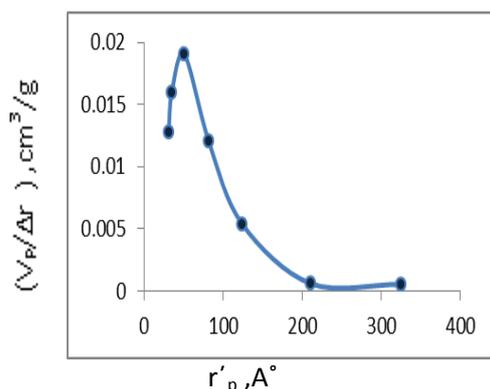


Fig.3, Pore size distribution of prepared Ni-Mo/ γ -Al₂O₃ catalyst

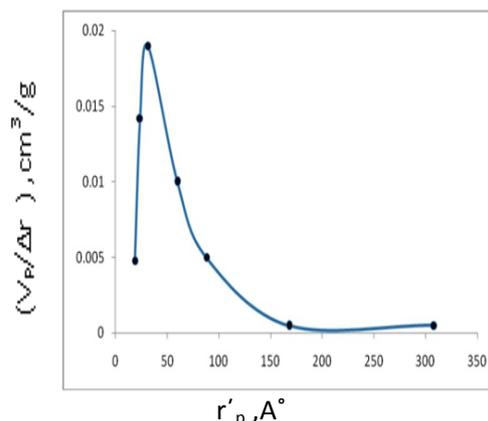


Fig.4, Pore size distribution of prepared Re-Ni/ γ -Al₂O₃ catalyst

3- Catalytic test

HDS activity of the three prepared catalysts was tested in hydrotreatment pilot plant.

Effects of Temperature and LHSV on sulfur removal

Figures 5 to 7 show the effect of temperature and LHSV on sulfur removal on three prepared HDS catalysts. It can be observed from the figures that Re-Ni-Mo/ γ -Al₂O₃ modified catalyst in general shows better sulfur removal than conventional catalysts (Co-Mo, Ni-Mo) at all the temperatures and LHSVs. This implies that the HDS activity of promoter's catalysts is improved the HDS activity, for example, at 325 °C and 2 h⁻¹, the sulfur removal is 55.9 wt. % for Re promoted catalysts, while sulfur removal for (Co-Mo) and (Ni-Mo) are 36.5 wt. % and 37.4 wt. % respectively, a decrease in LHSV from 2.5 to 1 h⁻¹ a better range for sulfur removal for all catalysts. Increasing the temperature generally leads to increase in hydrotreating conversion even at higher LHSV. This indicates that the rate of HDS is fast enough at higher temperature to mask the effect of increase in LHSV. The increasing of sulfur removal at high reaction temperature may be attributed to that the unreactive sulfur compounds which

most properly belong to thiophene derivatives become activated enough to react with hydrogen. Thus, the upper temperature value is limited by the undesirable side reactions such as hydrocracking reactions which are expected to occur at high temperature. As the LHSV increases sulfur conversion slightly decreases which means that the film diffusion has no effect on the reaction kinetics. The decrease in LHSV means that lesser quantity of gas oil contacting the same quantity of catalyst per time, while increasing in LHSV provides for a greater quantity of gas oil through the reaction per unit of time [13].

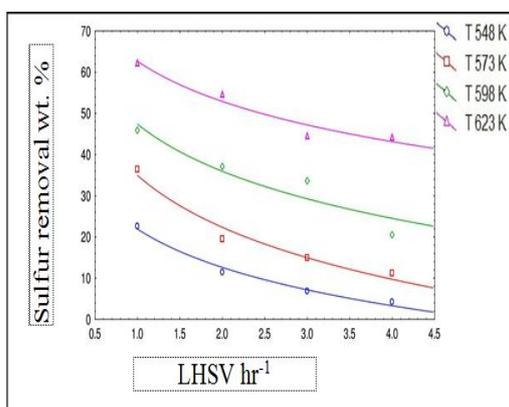


Fig. 5, Effect of LHSV on the sulfur removal of hydrotreated product for Co-Mo/ γ -Al₂O₃

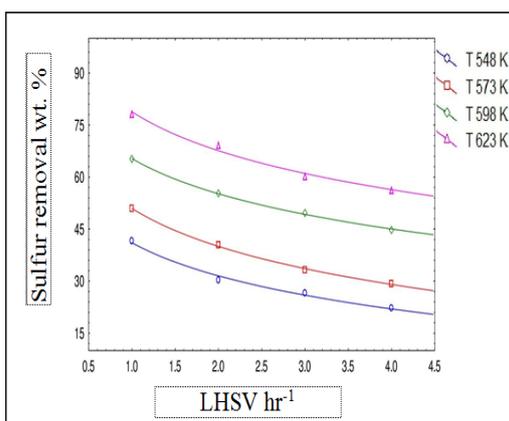


Fig. 6, Effect of LHSV on the sulfur removal of hydrotreated product for Ni-Mo/ γ -Al₂O₃

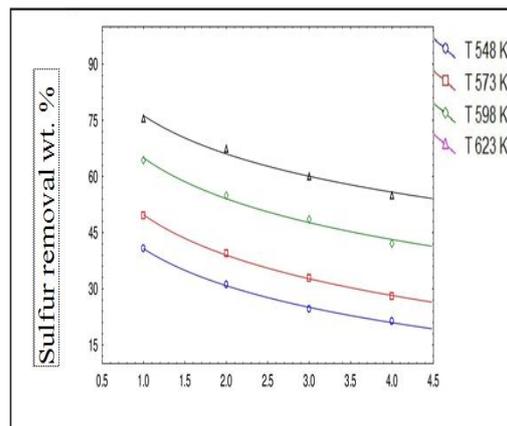


Fig. 7, Effect of LHSV on the sulfur removal of hydrotreated product for Re-Ni-Mo/ γ -Al₂O₃

Effects of Temperature and LHSV on Aromatic Content

Hydrogenation of aromatics may occur simultaneously in HDS process. Figures 8 to 10 show the aromatic content of the hydrotreated product.

These figures indicate that the aromatic content decrease with increasing reaction temperature and decreasing of LHSV. The increase of reaction temperature leads to increase rate of hydrogenation of aromatic and decrease the equilibrium constant, as mentioned by Girgis [14], while the LHSV decreasing leads to increasing the contact time. Also, as temperature increases, the aromatic compounds are decomposed into smaller one which can more easily diffuse into the catalyst macro and mesopores and reach the inner active sites where the desulfurization reaction mainly occurs.

Figure 9 shows that Nickel-molybdenum catalysts have a higher hydrogenation activity than cobalt-molybdenum (figure 8), at the same operating conditions, or greater saturation of aromatic rings. This means that increasing in residence time, which leads to offer a plenty of contact time of feedstock, with catalyst inside the reactor and lead to give a higher reduction in aromatic content.

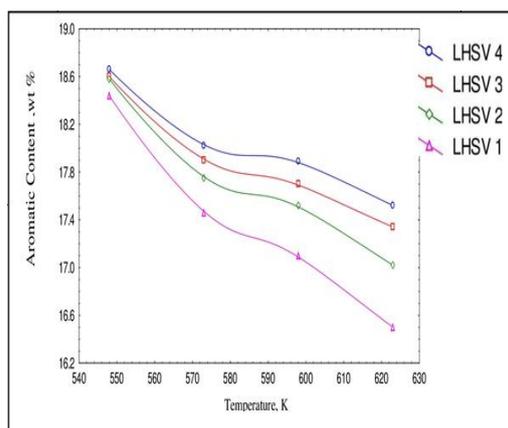


Fig. 8, Effect of temperature on aromatic content of atmospheric gas oil for Co Mo/ γ -Al₂O₃ catalyst

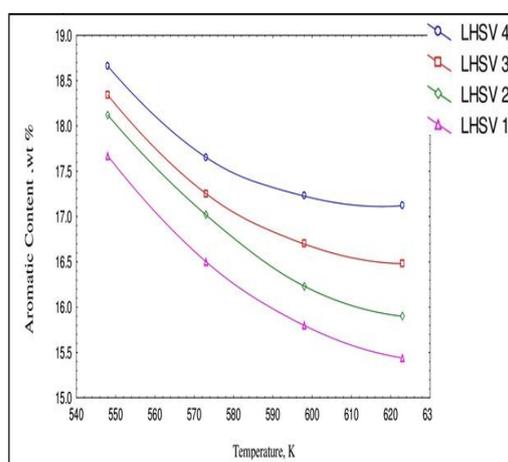


Fig. 9, Effect of temperature on aromatic content of atmospheric gas oil for Ni Mo/ γ -Al₂O₃ catalyst

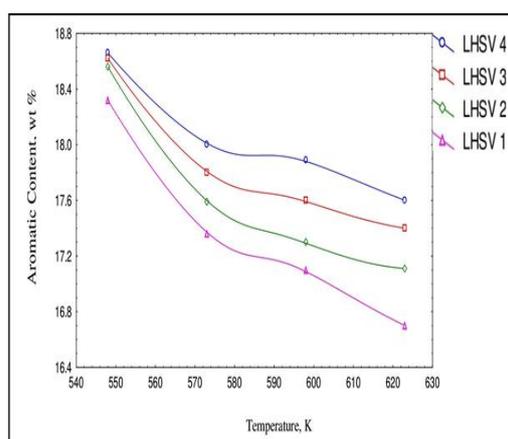


Fig. 10, Effect of temperature on aromatic content of atmospheric gas oil for Re Ni Mo/ γ -Al₂O₃ catalyst

Maximum aromatic reduction is achieved between (300–350 °C) because of the interrelation between thermodynamic equilibrium and reaction rates. For a given pressure, the optimum temperature is a function of the types of aromatic compounds in the feed and space velocity.

Conclusions

Hydrodesulfurization was improved when Ni-Mo/ γ -Al₂O₃ promoted with Re metals and consequent increase in activity, also Ni-Mo/ γ -Al₂O₃ catalyst is better for hydrogenation reactions than Co-Mo/ γ -Al₂O₃ and Re-Ni-Mo/ γ -Al₂O₃.

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