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Comparison between Conventional and Metakaolin bi-functional Catalyst in the Hydrodesulfurization Operation

Khlood S. AlKhafaji[1*], Bashir Y. Al-Zaidi[2], Zaidoon M. Shakor[3], Sattar J. Hussein[4]
[1,2,3]Department of Chemical Engineering, University of Technology, Baghdad, Iraq
[4]Ministry of Oil, Petroleum Research and Development Center (PRDC), Baghdad, Iraq
[1*]Corresponding Author E-mail: Khloodsalim1987@gmail.com

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Abstract

The present study investigates hydrodesulfurization (HDS) of gas oil with 9300 ppm (0.93 wt%) sulfur supplied from Al-Dura Refinery by using an economic catalyst prepared from raw mineral (kaolin clay) cemented by alumina as composite support alumina meta-kaolin (AMK). Characterization of the prepared catalyst was achieved by using Energy Dispersive X-Ray Analysis (EDAX), scanning electron microscopy (SEM), BET surface area, pore volume , Bulk density, X-ray diffraction analysis (XRD) and Fourier-transform infrared spectroscopy (FTIR). AMK was modified as a bifunctional catalyst with active metal (Co and Mo). The hydrodesulfurization (HDS) efficiency was evaluated and compared with the traditional catalyst (CoMo-Al2O3) in a hydrotreating reaction carried out in one stage reactor at temperature 375 oC, pressure 40 bar, LHSV 1hr-1, and H2/HC ratio 200 vol. ratio. 62.2% and 90% of hydrodesulfurization efficiency were achieved for prepared catalyst (CoMo-AMK) and commercial CoMo-Al2O3 respectively at the same operating conditions.

Keywords: Hydrodesulfurization, Kaolin, Alumina metakaolin, CoMo-AMK catalyst, Gasoil.

1. Introduction

The intermediate products of Iraqi crude oil, especially gas oil from crude oil of Basra and Kirkuk, contain high sulfur compounds ranging up to 14800 ppm and 12500 ppm for Basra and Kirkuk oil, respectively [1]. Gas oil consists of a wide range of hydrocarbons and removing undesired compounds represents a necessity to meet requirements for air pollution control. Hydro-desulfurization (HDS) is applied to reduce sulfur content to produce fuel with outstanding burning qualities by using highly active metal catalysts that permit the reactions to take place at mild conditions [2].

In addition, if the sulfur compounds are not removed it would lead to impairment of the final output specifications and the catalyst in the next units (such as catalytic cracking and reforming) will be subjected to poisoning. So, the development of new types of catalysts with highly hydro-desulfurization (HDS) activity is much desirable [3]. HDS Selective means converting organic sulfur to hydrogen sulfide by preservation of olefins. Mainly this concept which approach revolves around redesign a catalyst to be able to desulfurize and unsaturated the olefin. This can be complete by removing the active sites that saturate the olefin from the catalyst surface.

The end of this approach is that the sulfur has been changed to (H_2S), then olefins species are mainly preserved to prevent losses in fuel quality [4]. Usually, bimetallic catalysts based on the active phase and used different promoters (i.e. supported metal on alumina or silica) are used in industry to increase activity and selectivity for HDS of refractory sulfur-containing molecules [5].

The choice of catalyst mainly depends on the desired conversion and the characterization of the treated feeds. Ideal hydro-desulfurization catalyst most be capable removing nitrogen, sulfur and atoms of metal from streams of refinery and improve new a specifications fuel, such as the cetane or octane numbers and content of aromatics, which are necessary for high quality fuels and meet the standards of environmental legislation [6].

It is known that feed characteristics vary greatly and that the physical properties and the number of impurities determine and select the type of catalysts. This indicates that there is no universal catalyst or suitable catalytic system for hydro-processing feedstock from dissimilar sources, with concerning these physical and chemical properties, a wide range of hydro-processing catalyst had been advanced for commercial applications [7].

Commercial manufacture of HDS catalyst usually realized by simultaneous (supporter) impregnation of extrusion with aqueous solutions of ammonium heptamolybdate and cobalt salts or nickel nitrate, and the final catalyst activity is strongly dependent on the nature of the metal oxide phase achieved when impregnation and thus on the properties of impregnation the solution [8]. Vishwakarm used the impregnation and sonochemical methods to prepare catalysts with W (7 – 13) wt % and Co (1 – 3) wt % loadings based on γ- Al_2O_3 supported for HDS of middle distillates by a trickle-bed reactor. The catalyst performance after impregnation indicated maximum activity of the hydro-desulfurization reaction. The sulfur conversions were (93.0%) at 360 °C and 10.3 bar for (3Co - 10W)/γ-Al_2O_3. The interaction kinetics of the HDS were best fitted with a pseudo-first-order power law model with reasonable accuracy ($0.90 < R^2 < 0.95$) [9].

Mineral clays or modified mineral clays are used as commercial catalysts [10]. It has wide applications because its swelling, ion exchange properties, adsorption and high surface areas [11]. From the beginning of the petrochemical industries and petroleum refining, clays such as alumina silicate (zeolite) has been used as catalysts. Clays of different acidity can be obtained by calcining step (thermal treatment) prior to preparing the catalyst. The high temperature of calcining step the clay determines the concentration and type of hydroxyl group, and hence their acidity [12]. Clays supported on compound oxides of Al_2O_3 and SiO_2 having good catalytic properties and the ability to support by active metals and promoters [13]. The clay that is widely use in the preparation of catalyst is kaolin and has many applications such as synthesis zeolite [14] and gamma-alumina [15]. The ability to modify that clay by an active metals (metal oxide) or intercalation with plate anion, complexion materials, and organic chemicals represented a breakdown in the catalytic chemistry of these materials, as it presented new possibilities in mastering properties and interaction, although not fully explored [16- 17].

Most of the kaolin minerals are kaolinite ($Al_2Si_2O_5(OH)_4$) belonging to phyllo-silicates and ideally consisting of continuous sheets of tetrahedral and octahedral as shown in Figure **(**1). Each tetrahedral consists of a silica atom coordinated into four (O) atoms and bonds to the neighbouring tetrahedron by sharing three angles (basic oxygen atoms) to form an infinite two-dimensional "hexagon" mash pattern parallel to (x & y-axes). Each octahedral is formed from an Al atom and is coordinated by six oxygen atoms (Oxygen and OH) and is associated with octahedral dull by sharing edges [18].

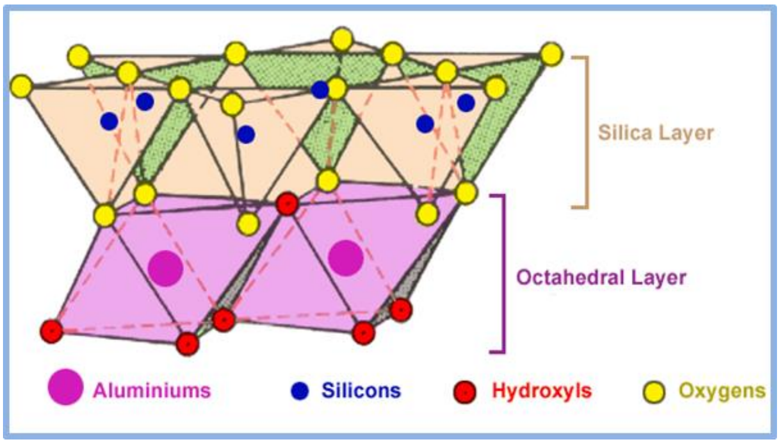


Fig. (1): Crystal structure of kaolin [12]

Although the kaolin clay has a low surface area, but it contains a layered porous composition of alumina and silica, which has possession of acidic sites that promote the activity of the catalyst, so this study aims to prepare and modify an economic support catalyst from kaolin clay, modified with active metal (Co and Mo) to prepare CoMo/AMK (Metakaolin bi-functional Catalyst) ($CoMoO_4/Al_2Si_2O_5(OH)_4$) then characterization the prepared was estimated in hydrodesulfurization reactions beneath processing condition held in packed bed reactor and compering with a commercial catalyst at the same condition to evaluate the efficiency of HDS operation.

2. Experimental Work

2.1 Material

Gasoil was supplied by Al-Daura Refinery (Midland Refinery Company) with a sulfur content of 9300 ppm. Kaolin clay (K) was received from Iraqi mining & geological commission, aluminum oxide (99% γ/Al_2O_3, with M. wt. = 101.96), Cobalt(II) Nitrate (97% $Co(NO_3)_2.6H_2O$, M. wt.= 291), Ammonium Molybdate (99.6% $(NH_4)_6MO_4O_{24}.4H_2O$, M. wt. = 1235) and sodium hydroxide (95% NaOH with M. wt. = 39.99) were supplied by BDH England.

2.2 Alumina meta kaolin support (AMK) preparation.

The Iraqi kaolin clays was selected as the raw material for the present study. Figure (2) shows that each sample was calcined at 600^oC for 4 h to get the meta-kaolin (MK) then the sample alkali treated was contains 20 gm of meta-kaolin powder mixed with NaOH powder in 4:1 a weight ratio. The sample was milled for 2 h crate to make, then homogenous mixture sample was calcined at 500°C for 4 h. The sample washed for 2 h with 200 ml by deionized water (DW) after calcined and immersed by water bath at 95°C. The suspension solution was filtered and the residue dried at 137 °C for over 10 h. Al_2O_3 and meta-kaolin powder with a weight ratio 50% for each were mixed together, then a certain amount of (DW) was added and stirred for 1 h. The suspension solution was dried for 8 h at 120 °C, then the sample was calcined at 550 °C for 4 h. The solids obtaine were referred to as AMK [19].

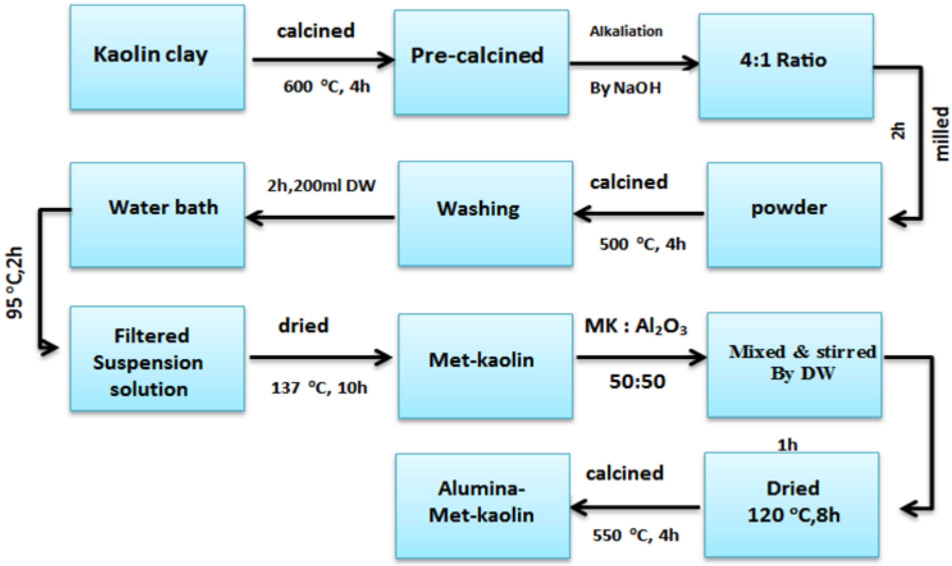


Fig. (2): Block diagram for the synthesis of Alumina Met-Kaolin.

2.3 Modifying Alumina -metakaolin by metal

By using wetness impregnation technique modifying metal/alumina metakaolin [20]. Loading the metal to ensure obtaining the desired loading percentage was carried out as in the following steps: preheating for alumina meta kaolin support at 250°C for 30 min in electrical furnace, the metal salt solution was prepared in a neck round flask 500 ml connected for impregnation apparatus, after that the support alumina metakaolin was added with stirring at 80°C for 4 h and the suspension washed with 1 L DW and filtered, then it was dried at 110°C 10 h, and calcined at 350°C for 2 h as stated in steps shown in Figure (3).

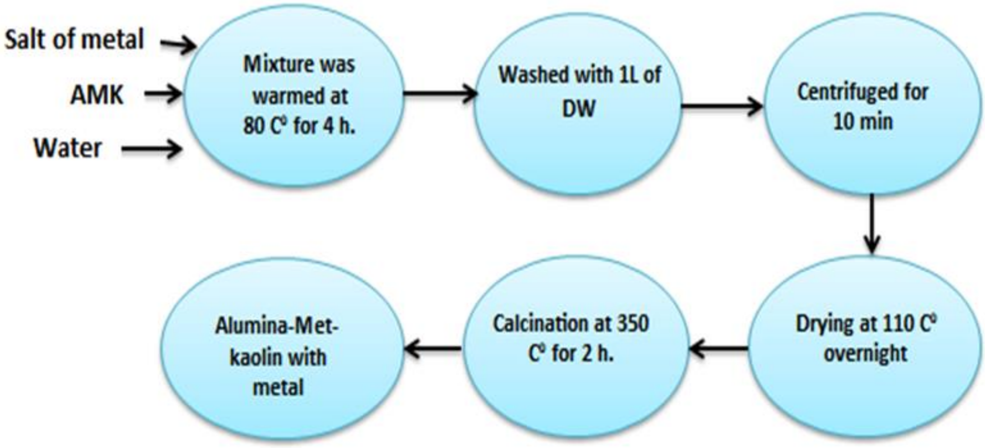


Fig. (3): Scheme show the procedure of prepare metal/AMK

2.4 Catalyst characterization

Energy dispersive X-ray analysis (EDAX] the identity of the elemental composition of materials by an x-ray technique and morphology analysis of catalysts were performed by scanning electron microscopy (SEM) instrument [Type: VEGA 3 LM, Origin: Germany] available at Department of Production Engineering Metallurgy /University of Technology. The specific surface area and pore volume using N_2 gas adsorption-desorption method at 77 k of catalysts was measured by using instrument [Type: Q-surf 9600, Origin: USA]. The instrument is available in the Petroleum R&D Center in Baghdad, Iraq. Bulk density is measured by (D-4164) according (American Society for Testing and Materials) method, instrument [Quanta-chrom, USA] located at Petroleum R&D Center. It determine by random place 40 cm^3 of catalysts in the cylinder inside diameter of 2 cm. Sulfur analyzer kind XOS was utilized to measure the concentration of sulfur in entrance and outlet streams. The analyzer model that used to measure overall the sulfur in crude oil products using the energy-dispersive X-ray fluorescence (EDXRF) method. This analyzer is proper for total sulfur revelation with a lower reservation limit of 1 ppm. The measurements were conducted in Petroleum R&D Center (PRDC) / Oil Ministry Baghdad, Iraq.

2.5 Experimental setup

The desulfurization unit shown in Figure (4), located in the Petroleum Research Center was used and to evaluate the activity of the catalyst prepared. Mainly the unit was composed of stainless steel vertical tubular reactor (1.75cm ID, 2.55cm OD and 30cm long) that is electrically heated in a double block furnace, temperature controller, gas meter, dosing pump, and high pressure separator. Hydrogen cylinder was supplied hydrogen gas to the unit. 40 g of the catalyst was charged in the reactor. The unit has been purified with nitrogen to ensure oxygen is removed from the unit; gradually the pressure was increased to 10 bar and continued for 5h to check for leaks. Hence, the nitrogen has been replaced with 99.99% purity of hydrogen. The catalyst was a hydrogen sulfide of the gas oil to convert the catalyst into a sulfide form (active phase). Pre-sulfates were performed at 220°C, 30 bar, 10 mL / min using untreated gasoil (sulfur contents of 9300 ppm) for 4 h. Aqueous desulfurization of gas oil was performed under operating conditions of 40 bar pressure, 1 h^{-1} LHSV, 375°C temperature and 200/ l liter hydrogen to hydrocarbon (H_2/HC) ratio. The products are collecting after the stabilization to reach a steady state.

Fig. (4): The experimental setup: (1) hydro desulfurization plant, (2) Reactor section, (3) Cooling system

2.6 Evaluating the activity of prepare catalyst

The fixed bed reactor shown in Figure (4), located in the Petroleum R&D Center was used and to evaluate the activity of the prepared catalyst. About 40 gm of CoMo-AMK was loaded into the middle part of the reactor, and the upper and lower parts were filled with ceramic balls with a layer length of 3 cm, 2 liters of gas oil as sample quantity was brought. Evaluation of catalyst activity for sulfur removal was conducted through two steps to reach the optimum result;

1- Drying process

The effectiveness of drying processes can have a large impact on product quality and process efficiency. Apart from the apparent requirements for drying solids for a subsequent process, drying can also be performed to improve the handling properties of the catalysts, as in the case of catalyst packing and other processes involving feed flow and for stabilization of moisture sensitive materials in heat- and mass-transfer processes [23]. The drying process was carried out using (10 Nl/hr) nitrogen gas at temperature (150°C) and pressure (10 bar) for (5 hr) to clean the unit from oxygen and check leaks.

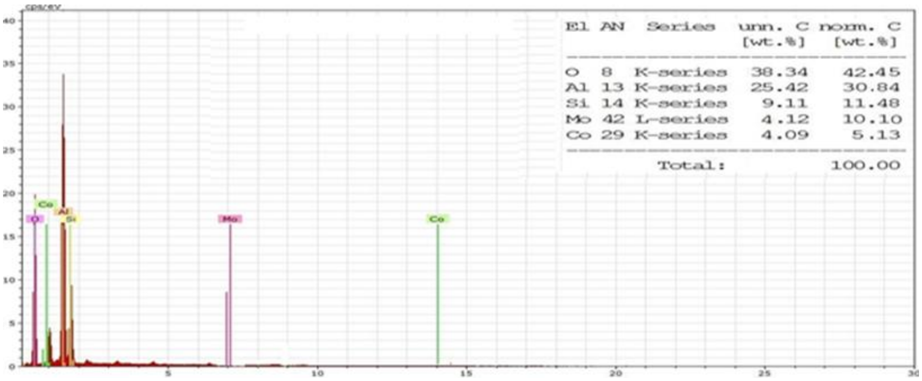
2- Sulfiding Experimental

Pre- sulfide was done at 30 bars pressure, 220˚C temperature by 10 Nl/hr Hydrogen gas for 4 hr. The sulfide operation includes passing a sulfide agent H_2 on the bed of catalysts in a carefully controlled procedure involving several temperatures. Where the agent is heated in the presence of H_2 to easily decompose the sulfur compound to form H_2S required to complete the sulfide reactions. So to complete the sulfiding process increase the temperature to (330°C) for (12 hr) to achieving maximum performance from their catalysts.

3. Result and Discussion

3.1 Energy Dispersive X-Ray Analysis (EDAX)

The way EDAX analysis works is that the electron beam hits the inner shell of an atom, knocking off an electron from the shell, while leaving a positively charged electron-hole. Second, its position is filled by another electron from a higher energy shell, and the characteristic X-ray is released [21]. Figure (5) shown the elemental composition of AMK after loading the active metal (5%Co and 10%Mo) by impregnation technique.



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]
O	8	K-series	38.34	42.45
Al	13	K-series	25.42	30.84
Si	14	K-series	9.11	11.48
Mo	42	L-series	4.12	10.10
Co	29	K-series	4.09	5.13
		Total:		100.00

Fig. (5): Typical EDAX spectrum for Co(5%) Mo(10%)/AMK catalyst.

3.2 Scanning Electron Microscopy (SEM)

The images of a sample produced by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the detected signal to produce an image [21]. Figure (6) shows images of kaolin before and after cementation by Al_2O_3 to produced AMK, it was found that there is a difference in the morphology after the alumina cementing process [22].

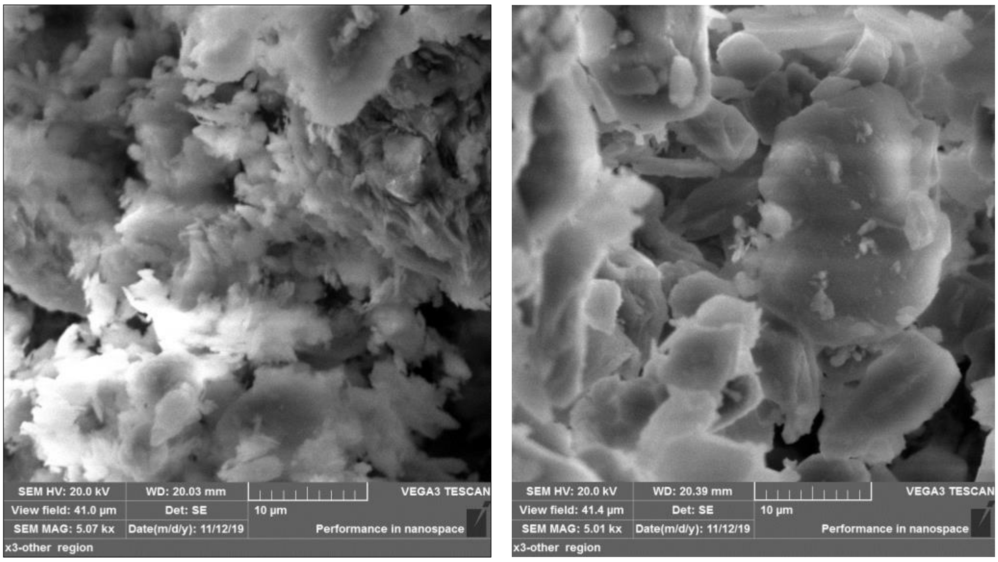


Fig. (6): Image of (a) kaolin clay, (b) AMK

3.3 BET Surface Area

Table (1) shows the surface area and pore volume of kaolin, AMK, CoMoAMK, and traditional catalyst (CoMo-Al_2O_3). The result shows the surface area of kaolin was increased after preparation of the AMK due to thermal treatment and cementing by alumina then decreases after modifying by metal, and the surface area of the traditional catalyst's brought. The surface area decreases after evaluation process of the prepared catalyst in a limited percentage due to the effect of the reaction of the removal process [19-23].

Table (1): The value of surface area and pore volume of sample

sample	Surface area m2/g	Pore volume cm3/g
K	36.6	0.064
γ/Al_2O_3	309	0.653
AMK	252	0.543
CoMo-AMK	213	0.325
CoMo-AMK (spent)	206	0.385
CoMo-Al_2O_3	183	0.360

3.4 Bulk density

It was determined by a random place 40 cm^3 of catalysts into a 2 cm diameter cylinder. The difference in weight between the cylinder filled with the catalyst and the empty one represents the weight of the catalyst. Bulk density is defined as the ratio of catalysts weight to sample volume. The bulk density of prepared catalyst (CoMo-AMK) was (0.914 gm/cm^3).

3.5 X-ray diffraction analysis (XRD)

X-ray diffraction analyses of of sample preparation for the analysis followed the methods of [24]. The results are presented in Figure (7) shows the XRD pattern obtained for cemented clay (AMK) by gamma alumina. The XRD pattern of cemented clay reveals the peaks confirm the presence accepted three strong standard peaks of gamma alumina with muscovite and quartz [25] (2θ= 26.88, 46.03, 67.22).

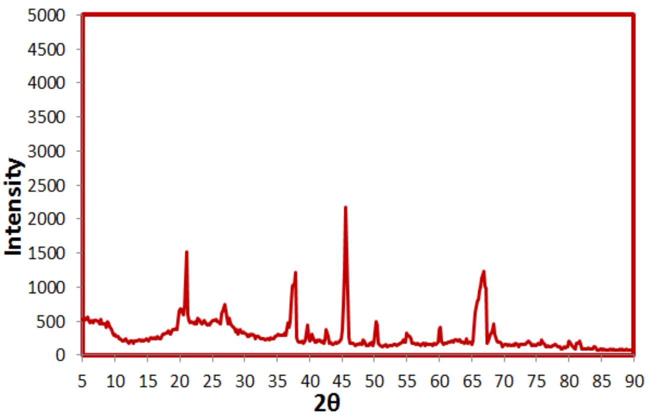


Fig. (7): XRD Patterns of prepare catalyst (AMK)

3.6 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of prepare catalyst is shown in Figure (8). Spectrum shows distinct peaks at 3692, 3650 and 3620 cm^{-1} corresponding to the vibration of OH-stretching. H-O-H characteristic peak was also found at 1290 cm^{-1} in the spectrum. The bands at 1052 and 1022 cm^{-1} can be assigned to Si-O bonds in the SiO_4 molecules. The other bands at 634 and 710 cm^{-1} are attributed to the vibrations of Al-O where the Al is in octahedral coordination. Peaks at 910 and 1634 cm^{-1}, corresponding to the expansion vibration(Co-O and Mo-O) respectively. The above results from the FTIR analysis are confirmation of the results of the EDAX analysis previously mentioned, as well as confirming that the impregnation process was carried out with the required accuracy. The results obtained are consistent with the publication of Granizo et al., [26].

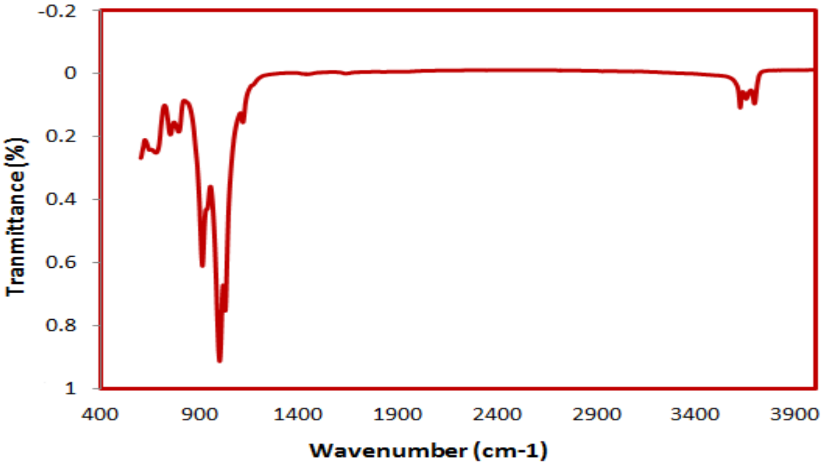


Fig. (8): FTIR spectra of CoMoAMK

3.7 Hydro-treating process

The hydro-treating of gasoil was done at temperature 375°C, LHSV 1 h^{-1}, hydrogen pressure was 40 bars and H_2/HC ratio 200 ml/ml. these conditions were applied on Iraqi gas oil feedstocks supplied from Al-Doura refinery in order to test the prepared CoMo-AMK efficiency to reduce the relatively high levels of sulfur content in feed to minimum levels as it is done with the commercial Hydrodesulfurization catalysts. The products liquid was collected after a 2 h stabilization period for run to reach the steady state from which sample was taken for sulfur content analysis.

The obtained result showed reducing the sulfur content in feed from 9300 ppm to 3512 ppm with HDS% about 62.2% as comparing with 90% for traditional catalyst CoMo-Al_2O_3 as shows in Figure (9).

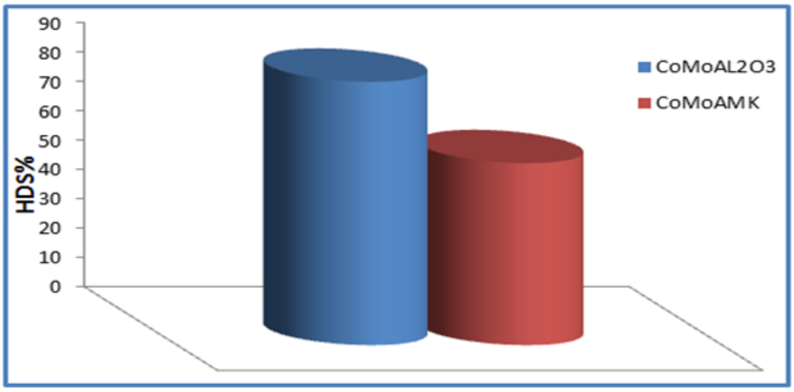


Fig. (9): HDS% of gasoil for CoMo-AMK catalyst and CoMo-Al_2O_3 catalyst.

375°C is the optimum temperature that also used in commercial process for sulfur removal in hydrotreating units, the high temperature leads to the increase of active internal molecular motions and it causes an increase in reaction rate to remove complex sulfur compounds [27-28].

Obviously, solubility of hydrogen in liquid increased at high pressure and more molecular hydrogen can be adsorbed onto the catalyst surface [29]. This phenomenon can be explained according to Henry’s Law, which state that the dissolution of a gas is proportional to its partial pressure above the liquid. Thus, increasing the partial pressure of H_2 will increase the concentration of H_2 in the liquid phase and thus enhance the hydro-treating activity, the pressure aim to break down the bonds between the sulfur compounds and the hydrocarbon molecules. Dropping the H_2 partial pressure below the design level deactivates the catalyst due to formation a coke [30].

A low value of LHSV indicates that lower volume of feed is reacted per hour and consequently large contact time of reactant with the catalyst used. Studies have been clarified lower LHSV to the half by increasing the catalyst volume to doubling lead to decrease the HDT reactor temperature and reach the same hydro-treating performance when the other conditions remain constant [31].

The surface area, pore volume, and pore size distribution directly effect on HDS operation, it is known that altering the surface functional groups present on the prepare catalyst during prepare step, for example by changing the octahedral layer after calcination step greatly effect on the reaction mechanism of HDS and thus the removal performance [32]. This was evident through the performance evaluation of the prepared catalyst in comparison with the conventional catalyst. We observed a lower hydrodesulfurization efficiency of the prepared catalyst, although it has a larger surface area compared to the conventional catalyst. Because of the properties of hydrogenation to prepare the catalysts, it has been negatively affected by the presence of types of superficial impurities on the catalyst, the most important of which is the Na, which was part of the preparation process (alkylation), as it has an effect on the dispersion and specific electronic properties of the active species along with its high surface area on the surface, considering that we use amorphous clay.

4. Conclusion

Cementation synthesis methods was successful in introducing Al_2O_3 into meta-kaolin (MK) to prepare alumina meta-kaolin (AMK) as a supports for HDS catalysts. Characterization techniques have shown that the presence of alumina affects the physical and chemical properties of the support catalysts (i.e. surface area, pore volume and thermal stability). CoMo-impregnated on AMK supports catalysts slightly decreases in surface area and the stability in surface area after evaluation of the catalyst. This bi-functional catalyst showed an efficient reactivity toward gas oil through adopting hydrogenation reaction in one stage reactor and the HDS% about 62.2%.

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