Design and Evaluation of a Co–Mo-Supported Nano Alumina Ultradeep Hydrodesulfurization Catalyst for Production of Environmentally Friendly Diesel Fuel in a Trickle Bed Reactor

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ABSTRACT: In the present work, a nanocatalyst, γ-Al2O3 nanoparticle-supported CoMo, was prepared experimentally and evaluated through a hydrodesulfurization (HDS) process for removing dibenzothiophene (DBT) from diesel fuel systematically in a trickle bed reactor (TBR). The results of the prepared catalyst characterization tests (scanning electron microscopy, X-ray diffraction (XRD), XRD phase quantification, and Brunner–Emmett–Teller) showed good distribution of active metals (CoMo), difference in surface morphology, and high dispersion of active metals. The catalyst exhibited good metal–support interactions without impacting the surface area significantly. A fully automated TBR reactor was used to evaluate the activity of the prepared catalyst in the HDS process at ranges of operating conditions: temperatures (250–350 °C), pressures (6–10 bar), liquid hourly space velocities (LHSV) (1–3 h⁻¹), and the activity of the prepared catalyst were compared to a commercial catalyst based on Co–Mo/γ-alumina. The results showed an obvious enhancement in the HDS process using the homemade nanocatalyst compared to the commercial catalyst. It has also been found that an increase in temperature led to an increase in the conversion from 68.77 to 91.57%, a little positive effect on conversion when pressure was increased, and a significant decrease in conversion (from 91.57 to 75.58%) as LHSV was increased. A kinetic model was developed for the HDS process to estimate kinetic parameters and apply the parameters in reactor design. The developed model showed that the DBT concentration in diesel fuel can be reduced significantly, 3000–240 ppm, at the optimum experimental conditions.

1. INTRODUCTION

Hydrotreating is a substantial finishing process in large refineries for reducing organic impurities and breaking down the high molecular weight of heavy petroleum feedstock in the presence of a suitable catalyst. The process of hydrotreating aims to raise the quality of petroleum to meet the environmental standards of minimal emission. Catalytic hydrodesulfurization (HDS) of crude oil and petroleum fuels is carried out at high temperatures and hydrogen partial pressures to convert organic sulfur compounds to hydrogen sulfides (H2S) and hydrocarbons. That, until now, alumina-supported Co or Ni promoted by MoS2 is still the most widely used hydrotreating catalysts in refineries was found in a previous study related to Co–Mo/Al2O3 catalyst in which alumina is not only an inert carrier but also a promoter ion. Since the first development of refining processes of crude oil, alumina is effective as a support for the HDS catalyst, and Ledoux et al. showed that γ-Al2O3 is the best among several supports in terms of HDS activity. They reported that the most effective one over η, θ, χ, or amorphous alumina was the γ phase, essentially owing to the impact of its surface orientation and crystallinity on the active phase. Moreover, it provides the acidic characteristics of the sulfide phase to improve the catalyst activity. Numerous researchers have found that Co–Mo supported on highly porous γ-Al2O3 prepared by the impregnation method is an effective catalyst combination for HDS of gas oil. The commonly used loading of the metals is 1–4 wt % for Co and 8–16 wt % for Mo. However, there are many drawbacks of using the conventional Co–Mo-supported alumina catalyst in the HDS process. One of the drawbacks is the formation of coke during the HDS process which reduces the catalyst’s lifetime and leads to a frequent and compulsory change of the catalytic bed in the reactor. Another drawback of using conventional catalyst is the strong interaction of the support with active metal oxides, which decreases the sulfidation yield. This can lead to a decrease in the surface area of the catalyst. Furthermore, conventional catalysts have a...
small surface area and pore volume that decrease the catalyst activity. Conventional catalysts appear to exhibit lower activity compared to nanocatalysts in the HDS process. All these concerns encourage research works on nano HDS catalysts. Metal nanoparticles (MNP s) have become most popular in the oil and petrochemical industry because of their excellent properties particularly catalytic properties. Also, in the chemical and oil industries, MNP-based catalysts play an important role. It is necessary to develop a novel catalyst to solve energy and environmental problems. Over the conventional catalyst support, nanoparticles with high surface area are widely used as catalysts for chemical transformations at present. For nanoparticles, the surface area plays a very important role in their catalytic properties. Rashidi et al. showed that the advantage of nanocatalysts is that they work under milder operation conditions (250–400 °C, 1–70 bar, liquid hourly space velocity (LHSV) 1–5 h⁻¹, and H₂/ hydrocarbon ratio 100–500 m³/m³) and a broad variety of hydrocarbon feedstocks. For confirming the chemical activity of the nanocatalyst in the HDS process, several researchers have used a batch reactor to obtain the reaction conditions necessary to achieve the highest conversion of dibenzothiophene (DBT). Yet, understanding the operating condition of HDS nanocatalytic reaction in a TBR, which is most widely used in an industrial reactor in the HDS process, is still lacking as all previous studies on HDS nanocatalysts were conducted in batch mode operation. This work contributes to a growing understanding of diesel fuel HDS. The HDS of diesel fuel using homemade Co–Mo/nano γ-Al₂O₃ is studied to determine the extent of sulfur removal and the performance of the catalyst. The HDS of diesel fuel using homemade Co–Mo/nano γ-Al₂O₃ is studied to determine the extent of sulfur removal and the performance of the catalyst. The results showed that the advantage of nanocatalysts is that they work under milder operation conditions (250–400 °C, 1–70 bar, liquid hourly space velocity (LHSV) 1–5 h⁻¹, and H₂/hydrocarbon ratio 100–500 m³/m³) and a broad variety of hydrocarbon feedstocks. For confirming the chemical activity of the nanocatalyst in the HDS process, several researchers have used a batch reactor to obtain the reaction conditions necessary to achieve the highest conversion of dibenzothiophene (DBT). Yet, understanding the operating condition of HDS nanocatalytic reaction in a TBR, which is most widely used in an industrial reactor in the HDS process, is still lacking as all previous studies on HDS nanocatalysts were conducted in batch mode operation. This work contributes to a growing understanding of diesel fuel HDS. The HDS of diesel fuel using homemade Co–Mo/nano γ-Al₂O₃ is studied to determine the extent of sulfur removal and the performance of the catalyst.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. The chemicals used for the preparation of the Co–Mo/nano Al catalyst are ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O, 99% purity, Sigma-Aldrich], cobalt chloride (CoCl₂·6H₂O, 99% purity, Sigma-Aldrich), and gamma alumina nanoparticles with specifications shown in Table 1 as received from the supplier (SkySpring Nanomaterials Inc.).

Table 1. Specifications of Gamma Alumina Nanoparticle

| specification                  | gamma alumina nanoparticle |
|--------------------------------|-----------------------------|
| pore volume (cm³/g)            | 1.5                         |
| bulk density (g/cm³)           | 0.333                       |
| surface area (m²/g)            | 487                         |
| particle shape                 | sphere                      |
| particle size (nm)             | 20                          |

The content of active metals in the nanocatalyst according to the present work is 3.5% Co and 11.2% Mo by weight. Cobalt chloride (14 g) and 148 g of ammonium heptamolybdate were dissolved in deionized water, and the solution was stirred by a magnetic stirrer for 1 h at room temperature to obtain a saturated solution. γ-Al₂O₃ particles (100 g) were added to Co and Mo solutions. Also, 2% of phosphoric acid was added to the impregnation solution to increase the acidity of the active sites by stirring for 1 h at room temperature until the particles were completely impregnated. The solution was dried in a furnace at 120 °C overnight; then the powder was calcined at 550 °C for 4 h. To pelletize the catalyst, 8% polyvinyl alcohol was used as a pelleting agent. The commercial HDS catalyst (3.5 wt % Co and 11.2 wt % Mo, surface area = 256 m²/g) used in this investigation was obtained from Baiji Refinery.

2.2. Textural Characterization of the Catalyst. The properties of the prepared catalyst were examined by different analysis methods. The Brunner–Emmett–Teller (BET) method was used to calculate the specific surface area and pore size of the prepared catalyst using a Sorptometric-1990 (CE Instruments, Italy). The N₂ adsorption/desorption method was used at the boiling temperature of liquid nitrogen (−195 °C). The samples were degassed at 300 °C in vacuum for 6 h. The volume of the adsorbed nitrogen was normalized to the standard temperature and pressure. The specific surface area was calculated by the BET equation applied to the range of relative pressures 0.05 < P/P₀ < 0.30 at the mesopore condition. The pore volume and pore sizes were determined using the BJH algorithm for adsorption and desorption of nitrogen. The cumulative pore volume was obtained from the isotherms at P/P₀ = 0.994. A D8 advanced X-ray Diffraction, Bruker, UK apparatus was used to analyze crystallographic conditions of the bulk phase of the catalyst sample and particle size. The software of this device is DIFFRAC plus-EVA ICDD powder Diffraction File Database, and it was used for data collection and manipulation. To examine the microstructure and quality of surface distribution of the active components, high vacuum FEI scanning electron microscopy (SEM, Quanta 200 FESEM, Switzerland) was used.

2.3. Catalytic Activity Evaluation. The feedstock used in this study was diesel fuel obtained from Petrol Office Company, Austria. The physical properties of the diesel fuel are shown in Table 2.

Table 2. Properties of the Feedstock

| property                      | value       |
|-------------------------------|-------------|
| specific gravity at 15.5 °C   | 0.8333      |
| kinematic viscosity at 40 °C  | 3.15        |
| flash point, °C               | 61          |
| DBT (ppm)                     | 9           |
| cetane index                  | 53.9        |
| color                         | 0.9         |
| pour point, °C                | −20         |

DBT has been used as a model compound in this work. DBT (99% purity, Sigma-Aldrich) was added to the feedstock to obtain a DBT concentration of 3000 ppm. Hydrogen gas (99.999% purity, Sigma-Aldrich) was used to hydrogenate the feedstock.

The performances of the homemade and commercial catalysts were evaluated in a fully automated trickle bed reactor (TBR), as shown in Figure 1. It is a set of catalyst activity detection devices. This TBR unit was manufactured by Zhejiang Finetec Instrument Company, China. The core of this unit was the tubular reactor which is made of a 316 L stainless steel tube, 100 mL volume (25 mm inside diameter), and 10 MPa maximum design pressure. The reactor was divided into three parts: the top and bottom parts contained ceramic balls and the space between them was loaded with the prepared catalyst pellets. The purpose of this arrangement of the ceramic balls was to provide a complete catalyst wetting, reduce radial dispersion, and reduce the bed porosity, thus...
minimizing any diffusion effects and providing plug flow conditions for isothermal reactions. The percentage of inert layers (ceramic balls) in the catalyst bed was between 30 and 35 vol %, and the catalyst loading was 30 vol %. The bed was dried at 120 °C for 1 h by a heating furnace made of a silicon carbide-aluminum high electric resistance alloy that surrounded the reactor (the max temperature was 500 °C, temperature control (±1 °C)). Heating was conducted in an atmosphere of hydrogen fed through a calibrated mass flowmeter (316L stainless steel pressure proof of 10 MPa, ±1% FS, Interface φ6) to get rid of any moisture from the catalyst. Then, the temperature was increased to 300 °C, and the diesel fuel was pumped into the reactor via a calibrated liquid metering digital pump (Walchem, Iwaki America Inc, USA, 0−40 mL/min, 316L stainless steel material) at a high rate of 5.0 h⁻¹ to presulfide the catalyst. The flow rate was then reduced to provide the desired LHSV according to the plan of experiments. The sulfided stream was then fed to a built-in 316L stainless steel pipe coil condenser outsourced with a 304 stainless steel shell and supplied with a φ6 double card sleeve pagoda type gas interfaces. Then, the product stream was sent to a gas−liquid separator made of 316L stainless steel to obtain the liquid desulfided diesel fuel and separate the hydrogen sulfide gas. Then, nitrogen was fed through the filter and via a reducing valve at a certain pressure to purge the system. The pressure difference before and after the mass flowmeter should always be controlled within 0.5 MPa (5 atm). The feedstock was prepared by adding DBT to hydrotreated diesel fuel (9 ppm total sulfur) with an initial concentration of 3000 ppm to evaluate the activity of the prepared catalyst. The reactor was continuously heated by the furnace; cooling water was arranged to flow through the heat exchanger to control the temperature. The temperature of the cooling jackets was not allowed to exceed 20 °C to prevent the vaporization of light components present in the diesel fuel. The experiments were conducted based on the full factorial design of experiments with the operating variables shown in Table 3.

The operation conditions temperature, pressure, and flow rate of the diesel fuel were maintained at a constant to obtain steady-state conditions. The product samples were withdrawn from the liquid outlet of the separator upon completion of the reaction, and the unit was set to shut down according to safety procedure. The remaining concentration of DBT in the product was measured by a high-performance liquid chromatography (HPLC) apparatus (JASCO HPLC System, UV-1575 UV/Vis Detector, Komasil C 18 reverse-phase column, 5 µm particle size, 150 mm length × 4.6 mm i.d., Japan).

2.4. Kinetics of the HDS Process. Usually, for the testing of a newly developed catalyst at a laboratory scale and to obtain intrinsic parameters of any rate of reaction, kinetic models can be used. There are several experimental proposals such as reduction of catalyst size, filling up the catalyst bed with inert fines, variation of the amount of catalyst, and flow rate to maintain a specific LHSV, and so forth. The only way to obtain kinetic information is to assume a kinetic model and adjust its parameter by comparing the model results with experimental data. The following assumptions have been made to develop a model for the HDS process using a nanocatalyst in a TBR investigated in the present study:

- The experimental unit is at steady-state operation.
- Pure gas is used (i.e. H₂) so that the gas side mass transfer resistance is negligible.
- The experimental reactor operates under isothermal conditions.
- Feed and products of the diesel fuel are in the liquid phase in the reactor.
- The liquid is always saturated with gas and gaseous reactants present in large excess; so the rate of HDS can be taken to be independent of the hydrogen concentration.
- Heterogeneous, one-dimension, with no axial dispersion operation.
- The catalyst is externally partial wetting while its pores are filled with liquid due to the capillary effect. Hence, no intraparticle temperature gradients are assumed to exist inside them.
- The pressure is constant throughout the reactor, and the “non-volatile” liquid phase is assumed under operating pressure.
- No change in the physical properties of the fluid due to reaction.
- The gas and liquid phases are considered as a pseudo-homogenous fluid for the energy balance (i.e. T_g = T_l) along the reactor.
- All the transport properties are well-distributed cross-sectionally and vary only with axial location and time.

Usually, for catalyst testing at a laboratory scale and to obtain intrinsic parameters of any rate of reaction, kinetic models can be used. Assume nth order kinetics for the chemical complexity of the reaction.

\[
-r_{\text{DBT}} = \frac{dC_{\text{DBT}}}{dt} = K_{\text{app}} C_{\text{DBT}}^n
\]  

![Image](https://dx.doi.org/10.1021/acsomega.0c00295)
where, $K_{app} =$ apparent reaction rate constant and $C_{DBT} =$ concentration of DBT at any time of the reaction. The reaction rate is constant for the HDS reaction, $K_{app}$ can be determined for each reaction using the modified Arrhenius equation as follows:

Arrhenius equation:

$$K_{app} = K_0 e^{-E_a/RT}$$  \hspace{1cm} (2)

In eq 2, $K_0$ is the pre-exponential factor or frequency factor; $E_a$ is the apparent activation energy of the reaction; $R$ is the gas constant; and $T$ is the absolute temperature.

$$-r_{DBT} = -\frac{dC_{DBT}}{dt} = K_0 e^{-E_a/RT} C_{DBT}^a$$ \hspace{1cm} (3)

Equation 3 will be solved for kinetics parameters through regression of experimental results of DBT concentration against the time of reaction.

3. RESULTS AND DISCUSSIONS

3.1. Catalyst Characterization. The X-ray diffraction (XRD) pattern of the alumina nanoparticles was obtained using an X-ray powder diffractometer (Bruker D8 EX-SITU XRD) with a pure Cu Kα1 parallel beam for high-resolution. The wide-angle scan was recorded with the 2θ range from 2 to 90° at a scanning rate of 1°/s. The wide-angle XRD patterns of Co-MO/nano γ-Al$_2$O$_3$ synthesized by impregnation are displayed in Figure 2.

The prepared catalyst exhibits well-determined diffraction peaks, marked as black, red, and blue at highest 2θ = 13, 27, and 68° for γ-Al$_2$O$_3$ nanoparticles, MoO$_3$ and Co$_3$O$_4$, respectively (ICDD Powder Diffraction file number: 190318H1_GA2). Also, it has been shown that the impregnation process gives the desired concentration of the metal oxides as 11.2% MoO$_3$ and 3.5% Co$_3$O$_4$ were achieved.

Figure 3 shows the SEM images and depicts the overall morphology of the prepared catalysts. It can be seen that the particles of the metal oxides were dispersed thoroughly on alumina nanoparticles due to the good mixing during the preparation, provided the impregnation method reveals good dispersion of Mo and Co particles. The uniform distribution of the metal particles on the surface of Al nanoparticles is beneficial for minimizing the agglomeration and increasing the catalyst activity.

Nitrogen adsorption−desorption isotherms and the pore size distributions of γ-Al$_2$O$_3$ nanoparticles impregnated with Mo and Co oxides were obtained as shown in Figure 4. The isotherm curve of the prepared catalyst resembles a type IV isotherm which goes very well with the layered nanostructure and implies surface adsorption. The adsorption−desorption cycle of nitrogen occurs at low relative pressure ($P/P_0 < 0.2$).
determining micropores structure with a pore diameter of 38.7 nm, adsorption cumulative volume of pores between 1.7 and 300 nm width: 0.41926 cm³/g. The BET surface area obtained is 435 m²/g, which is significantly higher than the commercial catalyst (256 m²/g). These results depicted a well-designed nanocatalyst.

3.2. Catalyst Evaluation. The experiments have been conducted in the TBR using cobalt molybdenum oxides over alumina nanoparticle prepared experimentally as a catalyst. The percent of error of measurement of DBT remaining after HDS was at the range of 1.65 – 8.74%. Measurement influence of reaction temperature, space velocity, and operating pressure are described as follows.

3.2.1. Effect of Reaction Temperature. The influence of temperature on the conversion of hydrogenation reactions of the sulfur compound is studied at 250, 300, and 350 °C at different space velocity (1, 2, 3 h⁻¹). Figure 5 shows the conversion of DBT obtained in the TBR using the homemade CoMo/nano γ-Al₂O₃ and commercial CoMo/γ-Al₂O₃ at 10 bar and (a) 1 h⁻¹, (b) 2 h⁻¹, and (c) 3 h⁻¹.

Figure 5. Conversion of DBT as a function of the TBR temperature for the homemade Co−Mo/nano γ-Al₂O₃ and commercial Co−Mo/γ-Al₂O₃ at 10 bar and (a) 1 h⁻¹, (b) 2 h⁻¹, and (c) 3 h⁻¹.

Figure 6. Effect of temperature on the process conversion of DBT for different pressures and (a) 1 h⁻¹, (b) 2 h⁻¹, and (c) 3 h⁻¹.

for instance, at 250 °C and 1 h⁻¹, conversion of 68.77% was obtained using the homemade CoMo/nano γ-Al₂O₃ versus 46.32% for the commercial catalyst (Figure 5a). The catalytic activity of the homemade CoMo/nano γ-Al₂O₃ was higher at 350 °C, where the efficiency of the chemical reaction became 91.57% for LHSV of 1 h⁻¹ versus 72.54% for the commercial catalyst at the same conditions. With an increase in hydrogenation reaction temperature, the efficiency increases significantly. The activity of the homemade catalyst does not decrease significantly at higher LHSVs, as shown in Figure 5b,c.

In Figure 6, it can be observed that as the reaction temperature increases from 250 to 300 °C, the conversion of DBT increases from 45.65 to 55.40% at 6 bar and 1 h⁻¹. The same trend was observed for the other operating pressures and LHSVs. Such behavior can be attributed to the following reasons:

- Increasing the temperature means that the number of molecules involved in the hydrogenation reaction will increase due to the increase in the activation energy. Besides, the diffusion and osmoses inside the pores of the nanocatalyst will increase with the temperature.26
also, the increase in temperature will have an influence on the physical properties of liquid feedstock with high impact. Henry’s constant and diffusivity will increase while viscosity and surface tension will be decreased. Thus, increasing the temperature and operating pressure promoted the absorption rate of molecular hydrogen into diesel fuel, the diffusing rate of DBT molecules, and the rate of dissolving hydrogen inside the catalyst nanopores to reach the active sites where hydrogen reaction occurs.27,28

- The phase change from liquid to the vapor of DBT takes place when the temperature increases from 300 to 350 °C (final boiling point of the feedstock is 357 °C).

Thus, the conversion of sulfur compound increased because of the molecules in the vapor phase having a high rate of diffusion inside the pores of the catalyst.29

3.2.2. Effect of Liquid Hourly Space Velocity. The influence of feedstock hourly space velocity on the conversion of DBT via the hydrogenation reaction was studied at 1, 2, and 3 h⁻¹ and is shown in Figure 7. It is indicated that operating at low space velocity could facilitate the conversion of DBT in HDS reactions. It is shown that the conversion of DBT decreased with the increase in reaction space velocity. This could be due to the short contact time between DBT and catalyst.30,31 A limited reaction of DBT occurred due to the small pores of the nanocatalyst that required operation with high pressure to enforce hydrogen and feedstock into the catalyst pores. At LHSV = 3 h⁻¹ and 6 bars, the conversion of DBT was diminished. Considering the obtained results, the optimal LHSV for the HDS reaction of DBT is 3 h⁻¹, which is the highest DBT conversion; 91.57% was obtained at LHSV = 1 h⁻¹, 350 °C, and 10 bar (Figure 7c). However, the conversion did not experience a significant drop as LHSV increased to 2 h⁻¹ as it maintained an 89.42% at 10 bar and 350 °C because operation at high temperature facilitated the chemical reaction of hydrogen and diesel fuel and minimized the influence of LHSV. This was also obvious at low hydrogen pressures of 8 and 6 bars where the difference in DBT conversion was significant at 350 °C and different LHSVs as they are 74–77% and 57–63%, respectively.

3.2.3. Effect of Pressure. The behavior of conversion of DBT as a function of pressure at different temperatures and LHSVs is shown in Figure 8.

The HDS of DBT is carried out at the range of 6–10 bars. These figures indicate that the conversion of DBT increases as pressures increases at all examined condition of the present study. This increase attributes to the positive impact of pressure on the gaseous reaction of hydrogenation as it is an

![Figure 7. Effect of liquid hourly space velocity on the process conversion of DBT for different temperatures and (a) 6 bar, (b) 8 bar, and (c) 10 bar.](https://dx.doi.org/10.1021/acsomega.0c00295)

![Figure 8. Effect of hydrogen pressure on the process conversion of DBT for different LHSVs and (a) 250 °C, (b) 300 °C, and (c) 350 °C.](https://dx.doi.org/10.1021/acsomega.0c00295)
reversible reaction. This impact becomes more obvious as temperature increases to 350 °C as the physical properties of the feedstock such as composition, density, and viscosity were modified. Thus, an enhancement from 57 to 89.43% was achieved as the operating pressure was increased from 6 to 10 bar at 1 h⁻¹ and 350 °C, which was to be expected due to the nanosize of the catalyst pores that are filled with a large excess of hydrogen available to hydrogenate DBT. Compared to operations with conventional Co–Mo catalysts, similar improvement was obtained but at a much higher hydrogen pressure of 25–35 bar.¹⁸,³¹

It can be seen from Table 4 that the homemade Co−Mo/nano γ-Al₂O₃ showed considerably higher activity compared to other catalysts reported in previous works.

### 3.3. Estimation of HDS Kinetic Parameters.

The following reaction rate law was generated via nonlinear regression of the experimental results to obtain the kinetic parameters shown in eq 3 for the HDS reaction over the prepared catalyst.

\[
- r_{\text{DBT}} = 2.36 \times 10^9 e^{(-51.72/RT)} C_{\text{DBT}}^{1.33} \text{[mol/cm}^3\text{h]}
\]

(4)

Activation energy according to the modified Arrhenius equation, a plot of ln K versus 1/T gives a straight line with a slope equal to \(-E_a/R\) from which the activation energy is calculated, as illustrated in Figure 9.

Several factors affect the activation energy, one of these factors is the type of the catalyst which is considered as the most important factor for the present study; the activation energy of DBT obtained over three different operating pressures (6, 8, and 10 bars) were different as 85.36, 61.78, and 40.535 kJ/mol, respectively. The second factor influencing the activation energy is the type of the solvent used; the activation energy of DBT in two different types of light gas oil over the same type of catalyst CoMo/Al₂O₃ at the same operation conditions were 108.68 and 112.86 kJ/mol in a previous study.³² The third factor affecting the activation energy is the type of the sulfur compound (individual or total) because HDS of total sulfur has higher activation energy than the individual; the activation energy for total sulfur of light gas oil was 119.966 kJ/mol in a previous study depending on sulfur compound contents in oil. So, the activation energy function of the type of catalyst, type of feed solvent, and the type of sulfur compound.

The order of reaction with respect to hydrogen gas is (0) for HDS of DBT that agrees with the assumption in Section 2.4 because of the little effect of changing hydrogen pressure gas.⁴,³⁵

### 4. CONCLUSIONS

The findings of the present study can be summarized as follows: using nanoparticles for the preparation of catalyst can exhibit high effectiveness in the catalyzed process of the HDS reaction compared to the commercial HDS catalyst. BET showed a large surface area for the prepared nanocatalyst in comparison with commercial catalyst, no change in the

| catalyst                          | reactor type            | operating conditions (°C) | sulfur content in the feed | conversion % | reference |
|-----------------------------------|-------------------------|--------------------------|---------------------------|--------------|-----------|
| Co−Mo/nano γ-alumina              | TBR                     | 350                      | 3000 ppm in diesel fuel    | 91.57        | present study |
| Mo−Ni/Al₂O₃ + AC                  | TBR                     | 300                      | 0.1 wt % in decalin        | 82%          | 36        |
| Mo−Co/CNT                         | fixed bed reactor       | 280                      | 1300 ppm in gas oil       | 73.5%        | 37        |
| Co−Mo/alumina                     | packed bed reactor      | 300                      | 4000 ppm in gas oil       | 67%          | 38        |
| Co−Mo/alumina                     | packed bed reactor      | 340                      | 300−400 ppm               | 98%          | 39        |
| Ni−Mo/alumina                     | packed bed reactor      | 350                      | 740 ppm                   | 90%          | 40        |
crystalline structure due to alienation and metal loading, a good percentage of active component appearance on the surface catalyst, and good distribution of active metals. The trickle mode operation with higher liquid hourly space velocity over the nanocatalyst did not impact DBT conversion significantly highest conversion of DBT achieved was 91.57% over the experimentally homemade prepared nanocatalyst (3.5% Co3O4-11.2% MoO3/γ-alumina nanoparticles) at reaction conditions of temperature = 350 °C, LHSV = 1 h⁻¹, and hydrogen pressure = 10 bar. The temperature used here is much less than the corresponding process with the conventional Co–Mo/nano γ-alumina catalyst which would reduce the operating cost significantly. Hydrogen can be used safely at optimum temperature in the TBR for catalyst nanoparticles giving excellent HDS reactions.

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**Notes**

The authors declare no competing financial interest.

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