



A Review of Nano-catalyst Applications in Kerosene Desulfurization Techniques

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Abstract

The production of clean liquid fuels is critical to maintaining a healthy life and environment around the world. To meet the new sulfur standard requirements, sulfur compounds must be effectively and completely removed from fuel oil. Therefore, researchers' attention turned to research into different techniques to remove sulfur from kerosene. This review focused on discussing a variety of catalysis approaches and emerging technologies for ultra-deep desulfurization of refinery streams for ultralow sulfur, such as hydrodesulfurization, catalytic-oxidative desulfurization, and adsorption desulfurization to form clean liquid fuels. This review discusses the most important industrial parameters that influence sulfur removal processes and has focused primarily on the main role of the catalyst and its type in impacting the efficiency of the process. Also, it will discuss the concepts of nano-catalysts, their preparation methods, and the most common forms, were described such as graphene, carbon nano-tubes (CNTs), metal-organic frames (MOFs), and zeolites. A comparison between the nano-catalyst and the conventional catalyst was also discussed to show the great effect of the nano-catalyst in improving the removal processes, which will lead to the development of innovative, efficient desulfurization methods that produce zero-sulfur fuels. In addition, understanding the most important challenges in nano-catalysts.

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1. Introduction

Kerosene, one of the petroleum products, was discovered by Abraham Gesner in 1853, is a clear, thin liquid that is formed from hydrocarbons with a density of around 0.78 to 0.81 g/cm³. It is obtained from the fractional distillation of crude oil between 150-275°C with a combination of carbon chains that contains between 6 and 16 carbon atoms per molecule, Sulfur is the 3rd abundant component after carbon and hydrogen in oil. Kerosene is commonly used in aircraft engines (jet fuel) and some rocket engines, also widely used as a fuel for cooking, heating, and lighting in rural areas where there is no power supply or it is too expensive for widespread use [1-5]. Sulfur compounds are the main issues in the refining industry. This has been attributed to the poisonous effect of these compounds on the upgrading desulfurization processes. The appearance of sulfur compounds in petroleum productions creates erosion in refinery equipment and poisoning of down-stream catalysts [6]. Moreover,

emissions SO_x from engines cause serious environmental pollution such as respiratory diseases and acidic rain [7, 8]. Around 3 million people die prematurely each year as a result of air pollution [6]. To reduce emissions, ever more stringent regulations were introduced for controlling a very low sulfur level in fuel oil. In the United States (USA), Sulfur content has been set at 30 and 15 mg/L, respectively. Since 2010, the maximum sulfur content in transportation fuels in Europe has been set at less than 10 mg/L [9]. This study focuses on comparing the most important sulfur removal techniques to reach the requirements of international legislation, as well as reviewing nano-catalysis and its impact on raising the efficiency of these techniques. The researchers' emphasis switched to discovering some ways to improve catalyst capacity to remove sulphur utilizing nano-catalyst as the impact on the effectiveness of the desulfurization process became apparent. In 1959, famous physicist Richard Feynman first described the ideas that started nanotechnology. The physical characteristics of nano-particles influence their catalytic behaviour, as well as how manufacturing conditions can change those physical attributes. If a scientist has a deeper understanding of nano-catalysts, they can create very active, selective, and robust catalysts. All of these benefits will make industrial chemical reactions extra resource-effective, lessen your energy consumption, and generate less waste; all of this will help to reduce the environmental impact of our reliance on chemical processes [10-14].

2. Typical Forms of Sulfur Compounds in Kerosene

Sulfur may be present in two separate forms in petroleum: "refractory sulfur" which comprises thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), and its alkyl derivatives. And "non-refractory sulfur," which includes sulfides, disulfides, and mercaptans [15, 16]. The sulfur concentration of liquid fuels varies by location, and as the oil well progresses further into production, sulfur removal becomes more difficult due to the high sulfur content. Crude oil can be found as "sour or sweet" depending on the degree of sulfur content; if the concentrations are greater than 0.5%, being termed "sour oil". [17-20]. Typical forms of sulfur compounds are summarized in Figure 1 [21].

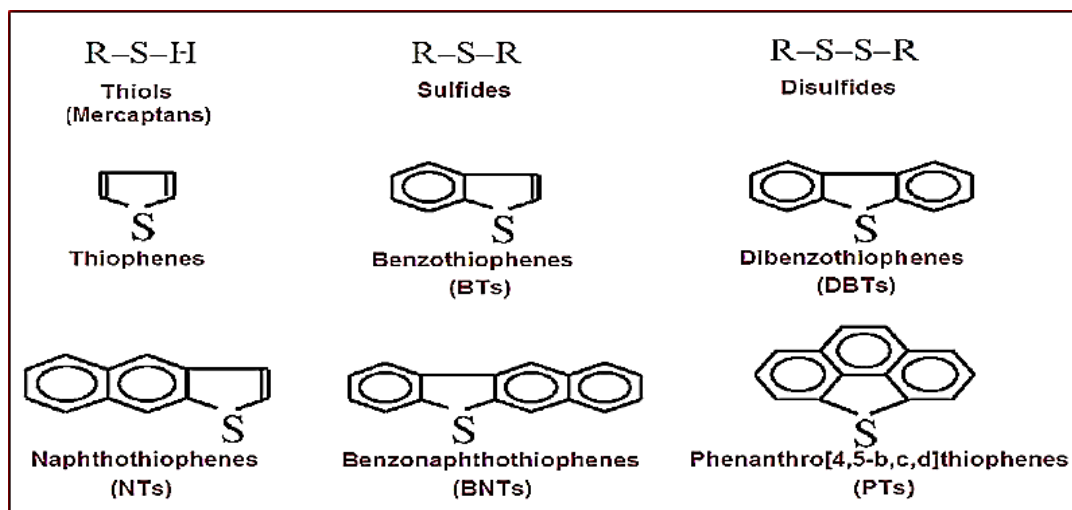


Figure 1: Typical forms of sulfur compounds [21].

3. Classification of Desulfurization Technologies

Sulfur removal methods are classified in various ways. They may be divided into three categories based on the kind of sulfur component eliminated, the method employed, and the influence of hydrogen (H). Also, the nature of the principal desulfurization process can depend. The first type relates to the most researched and commercialized catalytic technology, which comprises standard HDS, HDS with advanced catalysts and advanced reactor design, and HDS with extra chemistry to satisfy needs Fuel specifications, as shown in Figure 2. The second kind of desulfurization is focused on physical and chemical processes that are not intrinsically catalytic, such as oxidation desulfurization (ODS), distillation desulfurization, alkylation desulfurization, Absorption desulfurization (DSA), Extraction desulfurization (EDS), or a combination of these [22].

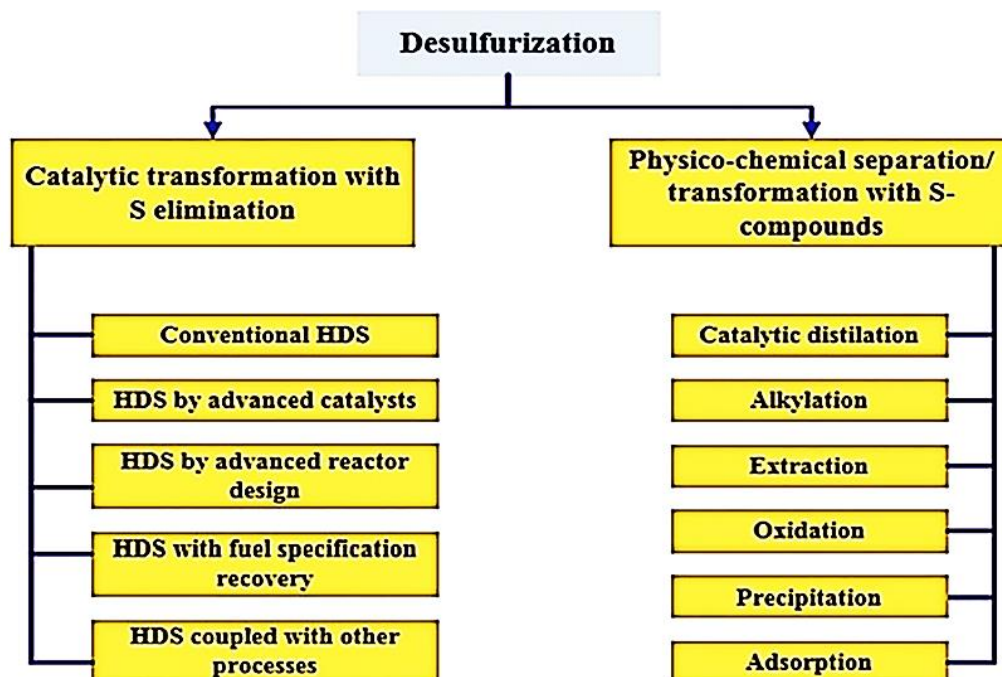


Figure 2: Classification of various desulfurization technologies Based on the role of hydrogen [22].

3.1. Hydrodesulfurization (HDS)

HDS is a well-known desulfurization process. It can handle a variety of liquid fractionation streams, from low to high boiling fractions [23]. In petroleum refineries, the traditional HDS entails mixing the input stream with hydrogen at a pressure of 7-150 bar and then heating it to a temperature of 300-450°C; these conditions are determined depending on the degree of desulfurization required. The mixture is forced to flow through a catalytic bed of metal oxides (usually cobalt or molybdenum oxides on various metal carriers), which aids in the formation of hydrogen sulphide (H_2S) by allowing hydrogen to react with sulphur [24]. A multitude of variables influences HDS performance, including operating parameters like pressure, catalyst type, temperature, and reactor design [23]. In Figure 3, the researchers studied two main factors, pressure and temperature, and their effect on the efficiency and performance of the HDS process and can be seen that increasing pressure and increasing temperatures improves the efficiency of the removal process [25].

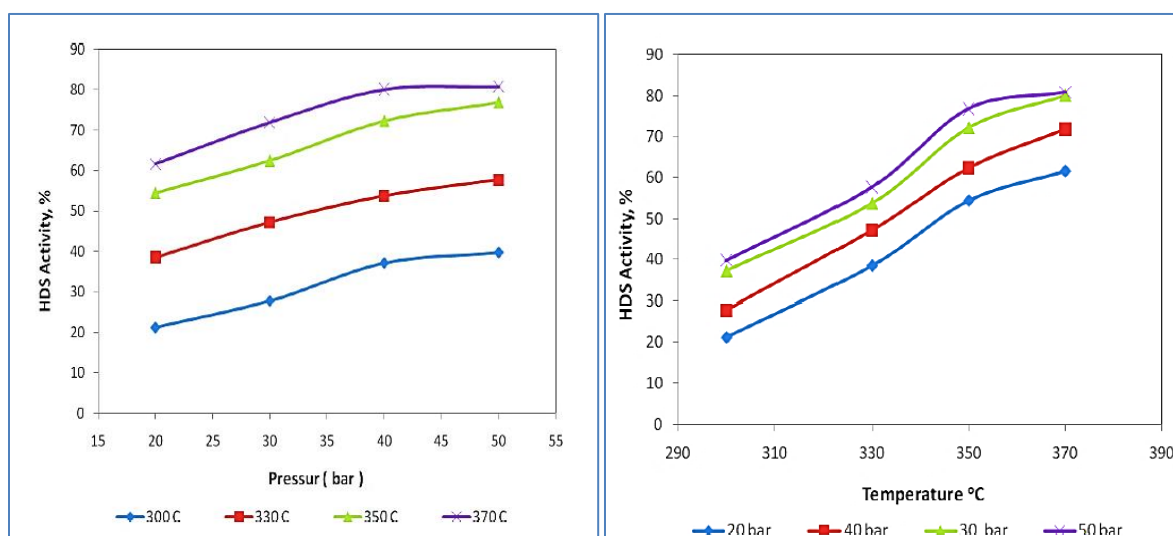


Figure 3: The effect of pressure and temp. On the removal efficiency of sulfur compounds by HDS desulfurization [25].

Hussein et al. Investigated HDS of raw kerosene containing (0.364 wt.%) sulfur, and (16.498 wt.%) aromatic components provided from Al-Dura Refinery. At varied circumstances, hydrotreating reactions were performed in an one-stage reactor over a high metal Ni W/ γ - Al_2O_3 produced catalyst. Sulfur components and aromatics were removed from 74.9 to 95.6% and 1 to 12.8%, respectively, under various operating conditions [26]. Behnejad et al. studied the two-step incipient wetness impregnation technique was used to create a bimetallic nickel-molybdenum catalyst assisted on alumina (Al_2O_3) in a fixed-bed microreactor. Efficiency tests were carried out at 45 bar for kerosene. The gross sulfur conversion for kerosene is 91.7% after 24 hours [27].

3.2. Adsorption Desulfurization (ODS)

An adsorption technique is commonly designed to provide selective sulfur compound elimination, work at ambient conditions with no difficulty of process control, attain high sulfur removal from fuel oils at a reasonable cost, and easiness of restoration with low chemicals and operating power, contrary to the HDS process [28]. Adsorption happens when a gas or liquid accumulates on the absorbent material's surface in a succession of phases. The adsorption mechanism is generally divided into four phases: (1) bulk diffusion, (2) film spread, or external mass propagation (diffusion across the boundary layer from the bulk fluid to the adsorbent (solid) surface), (3) Adsorbent pore propagation (intraparticle propagation): propagation from the adsorbent's outer surface into its pores. Adsorption between the active sites of the adsorbent (physical and/or chemical contact) [29]. Figure 4 depicts a basic adsorption procedure on a porous adsorbent [29].

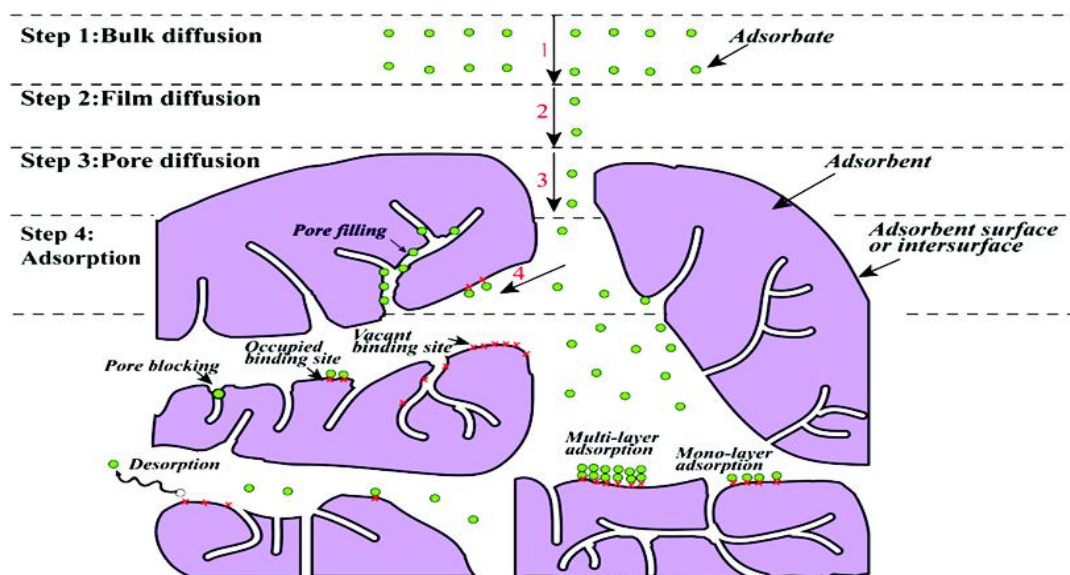


Figure 4: procedure of adsorption on porous sorbents [29].

ADS efficacy is determined primarily by the textural properties of the adsorbent. The desirable properties are large surface area and pore volume. Moreover, higher numbers of active sites, mechanical hardness, and thermal stability are all desirable characteristics [30]. Adsorbents could be categorized into two forms: natural and industrial. Zeolites, charcoal, clays, and clay minerals are examples of natural adsorbents. Industrial adsorbents contain activated carbon, silica-gel, activated alumina, molecular sieves, etc. [31]. ADS may be divided into two types based on the method of the sulfur compound's interaction with the sorbent: Physisorptions when sulfur compounds are removed by physical processes (interactions of Van der Waals forces) rather than a chemical action, and the Chemisorption where the sulfur compounds are removed by chemical treatment. The selectivity of sulfur is not regulated by physical adsorption and the π -complexation interaction is more efficient than the forces of van der Waals, allowing sulfur compounds to be selected more easily than other compounds. To overcome selectivity and diffusion limitations, various physical and chemical adsorbents were investigated. It's also worth noting that the majority of adsorptive desulfurization study has been carried out in batch experiments. Metal incorporation, as well as acid or alkali treatments, were found to substantially increase adsorbent adsorption capacity by boosting active sites on the surface for acid-base and direct sulfur-metal bindings [32].

The main parameters influent of adsorption desulfurization that the researchers discussed are the adsorbent dose, contact time, initial sulfur concentration, PH, and temperature. Figure 5 shows the effect of temperature, a dose of adsorbents, and contact time on the removal rate [33, 34].

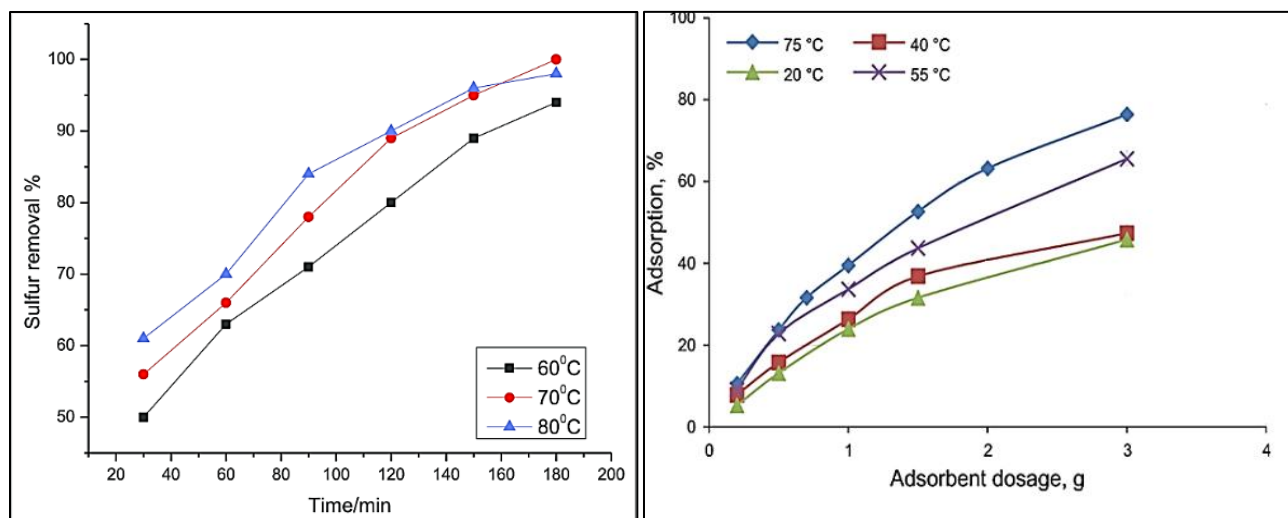


Figure 5: The effect of time, adsorbent dose, and temperature on the removal efficiency of sulfur compounds [33, 34].

3.3. Catalytic Oxidation Desulfurization (CODS)

This process has been considered the most promising method because of its mild operation conditions, and in comparison, to the HDS, it has a higher selectivity in removing aromatic sulfur compounds. Additionally, it does not need the acquisition of expensive hydrogen [35]. Early studies on the CODS technique were conducted utilizing (NO_2) as an oxidizing agent and methanol as solvent. From that on, other oxidizers have been tested like H_2O_2 , HNO_3 , N_2O , NaClO , NaClO_2 , NaBrO , and PhIO . The oxidizer gives O_2 atoms to the S-compounds to generate sulfones or sulfoxides. Among all the oxidants mentioned, H_2O_2 has been the best candidate. It is characterized by low cost, environmentally friendly, and availability. The major drawback of utilizing H_2O_2 is the slow rate of reaction [36]. Peracids are extremely potent oxidizing agents that may easily oxidize refractory sulfur compounds. These substances are corrosive and extremely reactive [37]. Separation is made more difficult by the presence of an oil-soluble natural acid in the reaction media. Also, organic acid catalysts that are oil-soluble are non-renewable and cannot be fully recovered. To improve the efficiency of this process, several catalysts were utilized and transition metal salts are the most commonly used, particularly tungsten salts [38, 39], in the oxidation of sulfur with peracids, they are very active and selective. Iron salts are also a good option since they can generate ($\text{R-COOO}\cdot$) radicals from peracids, which are extremely reactive and have a large oxidation capacity [40]. A second option is the use of altered activated carbon as a catalyst to promote the oxidation reaction [41]. Omar G. Hammoodi et al. [42] used a nano-composite cobalt ferrite/graphene ($\text{CoFe}_2\text{O}_4\text{-G}$) which was synthesized by sol-gel technique. The composite was utilized to remove sulfur from the Iraqi kerosene with concentration of about 500 mg/L. The authors revealed that removal performance was higher than 90% at optimum conditions. Vu et al. [43] prepared a composite material of carbon nano-tubes (MWNTs) and TiO_2 . Where they have surface areas of $17.32 \text{ m}^2/\text{g}$ and $8.44 \text{ m}^2/\text{g}$, respectively. The results show that the DBT conversion of MWNTs/ TiO_2 composite is 80%, and that of pure TiO_2 is only 56%. The major reason is that pure TiO_2 is easy to accumulate and its specific surface area is limited, resulting in fewer active sites, which directly limits the performance of the oxidation desulfurization process.

4. Conventional Catalyst in the Desulfurization Process

Metal oxide-based adsorbents were studied because they offer several attractive characteristics, including simplicity of synthesis, high framework stability, and chemical solvent insolubility. Al_2O_3 , SiO_2 , ZnO , and TiO_2 are some of the most prevalent metal oxide adsorbents. Al_2O_3 has piqued the interest of researchers due to its inexpensive cost, widespread availability, and ease of synthesis. Doping transition metals, such as Ag, Cu, Zn, and Ni, into metal oxides has been discovered to have a considerable favourable influence on adsorption capacities.

[32, 44]. Also, zeolites and their metal-loaded derivatives are being used as sorbents in a variety of applications because of their large surface area, pore size, three-dimensional structural, and structure charge. They can easily be filled with transition metal ions due to their negatively charged structure, making them a good candidate for adsorptive desulfurization [45]. Velu et al. [46] reported (NH₄-Y) zeolites (Y) with transition metals including Ce, Zn, Pd, Ni, and Cu demonstrated preferential organic sulfide adsorption. Ce-exchanged NH₄-Y zeolites showed higher selectivity for sulfur compound adsorption as compared to aromatic selectivity. They indicated that the sulfur compounds were removed by immediate sulfur-metal (S-M) interaction instead of complexity. Oliveira and colleagues [47] the researchers evaluated the adsorption capability of Thiophene and Toluene on Na-Y zeolites exchanged with transition metals (5 wt.% Zn, Ni, and Ag) as well as their competitive adsorption behavior. The results showed that transition metals should be inserted into the structure of zeolite to improve the adsorption of sulfur compounds and aromatics in the organic liquid mixture. Another adsorbent employed is carbon, analogous to a "molecular sponge." Commercial activated carbons have surface areas of above 400 m²/g, with several exceeding 1000 m²/g [48] so are used as a catalyst or as adsorbents in various industrial processes [49]. The raw materials that are most commonly utilized are (i) All types of coal, (ii) coconut shells, (iii) wood, (iv) peat, and (v) petroleum-based residues. The carbon source chosen is determined by the desired characteristics of the finished carbon [50]. Although all types of AC are created from organic parent materials, the carbonization and manufacturing procedures differ. Activated carbon is available in powder, granular, and pellet form on the market right now. It is classified into different types based on particle size and shape, with each variety having its unique set of uses [48, 51]. Shah et al. [52] studied experimentally the performance of tin-doped-activated charcoal (Sn-AC) as an efficient adsorbent for the desulfurization of real straight-run kerosene and diesel oil types. The first set of experiments was conducted utilizing model oil, prepared by using dibenzothiophene (DBT) in cyclohexane; the best performance obtained was 99.4%. Suryawanshi et al. [28] studied metal modifications and their impact on sulfur elimination selectivity. For their experimental setup, they used two adsorbent types, a commercial TAC, and the other was a homemade prepared from Cassia fistula biomass. Single and bi-metal impregnation was investigated using Zn, Co, Ni, and Cu. Moreover, ultra-sonication was coupled with adsorption to further enhance sulfur elimination. The authors reported that the combined influence of metal impregnation and ultra-sonication could highly enhance sulfur elimination.

5. Nano-catalysts

Catalysts and catalytic processes have long been catalytic chemistry's "Holy Grail". Over the last century, catalytic research has revealed that the main primary steps of catalytic reactions (reactant adsorption, intermediate diffusion, and product desorption) all require the transfer of electrons between the catalyst surface and reactive particles. The theory of boundary molecular orbitals can explain the main stages in surface catalytic processes. According to the hypothesis, the intensity of adsorption and binding of reactants on the catalyst surface is determined by the symmetry and rotational state of the reactant's molecular or atomic orbitals and the alignment of the reactants' energy levels with the levels of the catalyst surface [53]. Greeley and coworkers [54] invoked the so-called d-band center hypothesis, which confirms that the density of valence electrons in the d-band at the Fermi level is an important factor influencing catalytic reactions. In the meantime, the unique chemical and physical properties of nano-particles (NPs), which appeared with the development of nano-science, have aroused interest in various fields, including catalysis [55, 56]. When a bulk substance along a path is reduced to a nano-meter scale, the transport of electrons along that path is constrained by valence electrons, which generate continuous bands in bulk metals. Nano-particles have substantially larger overall exposed surface features and a variety of surface patterns than bulk metals. The impact of electron trapping inside nano-particles can create significant alterations in the electrical structure enabling fine-tuning of the catalytic process. In this way, nanotechnology will enable us to alter the surface structure and electronic characteristics of supported Nano-catalysts in a quantifiable and effective manner without affecting their content. As a result, it is expected that improving absorption and catalytic interactions would be possible by altering catalyst size on a nano-scale. Size effects in NPs have been seen in catalytic studies since the beginning, for example, in research on ultrafine particles and single-site catalysts [57–61]. It is been known for a long time that catalytic activity rises as catalyst particle size decreases. Furthermore, it was previously considered that a reduction in particle size simply resulted in a raise in the proportion of catalytically active surface species as well as an increase in surface defects; these factors were thought to be the primary causes of the size effect. However, as nano-science has progressed, it has become clear that Catalytic NPs reveal quantum size effects in their electrical nature, in addition to increased surface area and atomic heterogeneity. Additionally, the electrical confinement effects of nano-scale pores are unique [62–64]. As a result, the

combination of nano-science/nanotechnology and catalysis opens up a world of possibilities for catalysis advancement. Nano-particles may be made using a variety of methods that fall into two categories: top-down technologies and bottom-up technologies as shown in Figure 6. [65]. There are several methods to synthesize supported nano-particles, including microemulsions with an organic stabilizing agent, Impregnation, deposition-precipitation and co-precipitation, sono-chemical reduction, chemical vapor impregnation, and sol-gel [66].

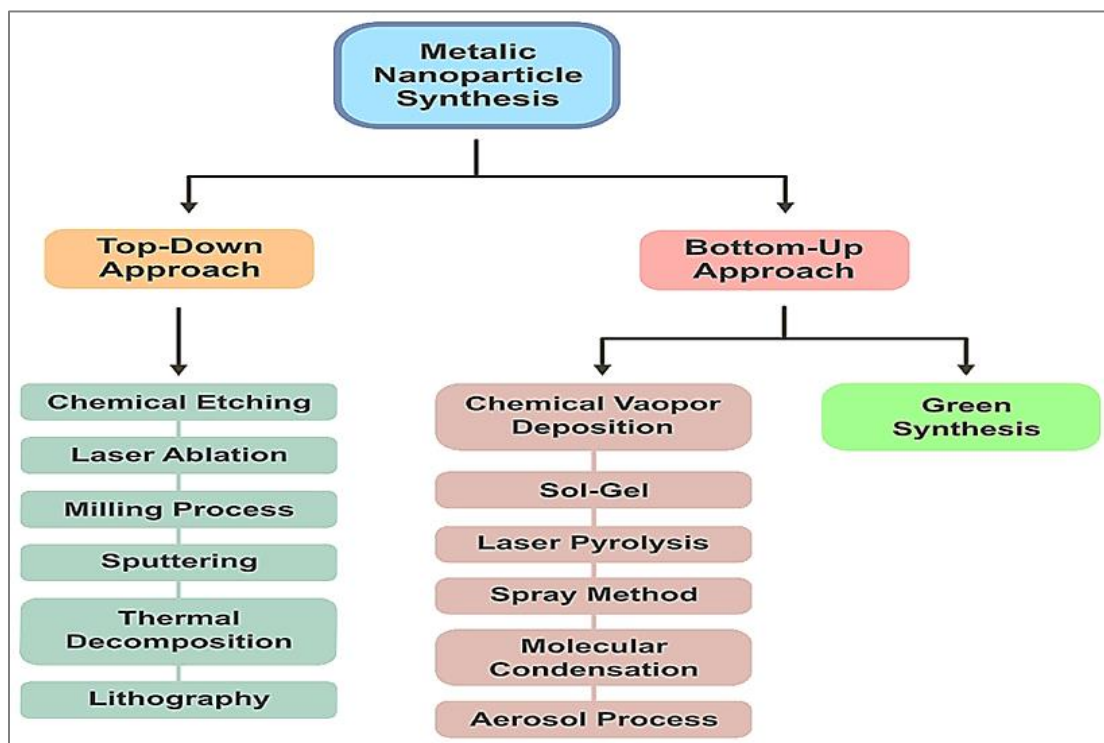


Figure 6: Two main methods of synthesizing nano-particles [65].

The influence of intrinsic characteristics of nano-particles on catalysis may be understood by examining the underlying concept of nano-catalysis. Quantities that are connected directly to bond lengths, like the mean lattice constant, atomic density, and binding energy, are intrinsic features of nano-materials that have a significant influence on their catalysis activity. Densification and surface relaxation are caused by lattice contraction in a nano-solid. (i) Self-organization growth, thermal stability, Coulomb blockade, phase transition threshold temperature, and evaporation in a nano-solid. The activation energy for atomics dislocation, diffusion, and chemical reactions is determined by the coherent energy per separate atom. (ii) The band structure as a whole, as well as related features like band gap, photo-absorption, core-level energy, photoemission, and quantum well, are determined by characteristics that change with the binding energy intensity in regions of relaxed continuity, like the Hamiltonian. (iii) Mechanical toughness, Young's modulus, extensibility, surface stress, surface energy, and compressibility of a nano-solid, as well as the magnetic effectiveness of magnetic materials nano-solid, are all attributes derived from the cumulative effect of binding energy density and cohesive atomic energy [67]. For many years, many metals and minerals as instance aluminum (Al), clay, iron (Fe), titanium dioxide (TiO₂), and silica have all been utilized as catalysts on the nano-scale [68]. However, the proper explanation for the remarkable catalytic activity demonstrated by NPS is still unknown. Nano-particles with a large surface area have a direct beneficial influence on reaction rate, which might potentially be a plausible explanation for their catalytic activity. The catalytic activity can be influenced by the structure and shape-based characteristics of any substance on the nano-scale. Nano-catalysts have been fine-tuned in size, shape, and composition (usage of supports, core-shell type, or bimetallic) resulting in increased selectivity. As a result, the focus of the topic is on how the physical characteristics of nano-particles influence their catalytic characteristics, as well as how manufacturing parameters influence those physical attributes [69, 70]. For Comparison between conventional catalyst (homogeneous, heterogeneous) catalysts and nano-catalysts. Each kind has unique features. Homogeneous catalysis is characterized by its high activity and high chemical selectivity, but the apparent drawbacks are the cumbersome

purification of the product and the difficulty of recovering the catalyst. As for heterogeneous catalysis, its advantages are easy recovery, high stability and seamless separation. However, its numerous benefits do not make it perfect as it necessitates a long reaction time and low catalyst activity [67, 71]. Nano-catalysts incorporate the benefits of both homogeneous and heterogeneous catalytic systems. Fast, selective chemical transformations with good product yield are possible using a nano-catalytic system, allowing easy catalyst separation and recovery. The interaction between reactants and catalysts rises substantially due to nano-size (high surface area) because of its dissolvability in the reaction solvent, easily removed from the reaction mix [72].

6. Common Nano-absorbents in Desulfurization Processes

6.1. Zeolites

Zeolites ignited a revolution in the field of catalysis due to their unique structure and performance, so it has vast catalytic application areas. This material has a high activity, a substantial adsorption capacity, a large surface area, and pores with diameters from 2 to 50 nano-meters rang. These characteristics improve adsorption and catalysis performance; wide pores allow the formation of large molecules, which may then be chemically changed in a variety of ways; and metal exchange/impregnation can affect the surfaces for successful deep desulfurization. Conventional meso-porous materials (for example, silica and alumina) have a homogenous distribution of meso-pores as shown in figure 7. The two of the most popular commercial meso-porous materials are MCM-41 (a hexagonal array) with a pore diameter of typically 2-4 nm and SBA-15 (analogous to MCM-41) with a pore diameter of 4.5-30 nm [73-78]. Ko et al. [79] and Park et al. [80] investigated the SBA-15 nano-material and modified it for the desulfurization process by adding nickel metal in varied weight ratios. Loading 30% of the nickel at a sulfur level of 10 mg/L resulted in a penetration capability of roughly 1.7 mg/g. Shalaby and coworkers [81] also reported meso-porous materials SBA-15 and MCM-48 modified with nickel and evaluated the metal loading impact on SBA-15 and MCM-48 by using ultrasonication for enhanced nickel dispersion on a support surface. Desulfurization was conducted in a fixed-bed flow reactor sorption system at 220C° for sulfur concentration 14.5mg/L (4, 6 DMDBT) with (20 wt.% Ni) loading on MCM-48. They have been found the adsorption capacity of 2.1 mgS/g at a sulfur content of nearly 1mg/L. Also, (DBTs) are adsorbed on the surface of SBA-15 and MCM-48, probably by contact between the S atoms in the sulfur compounds, the exposed Ni atoms on the surface, and a part of the adsorbed alkyl (DBTs). The Ni/SBA15-breakthrough capacity was produced without the use of ultrasonics by employing the incipient wetness impregnation (IWI) technique.

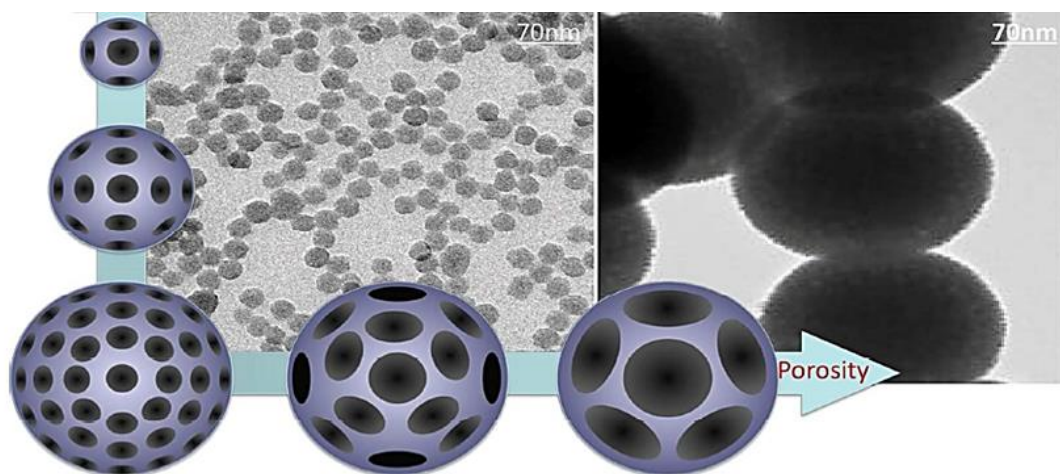


Figure 7: Nano-structured meso-porous material [73].

6.2. Metal-Organic Frameworks (MOF)

Metal-organic frameworks (MOFs) have been more critical in the area during the last decade. MOF comprises a combination of inorganic and organic components and is described as a porous 3-dimensional structure consisting of metal sites or clusters related by organic bonds. It is also having a modular design that distinguishes it from other porous materials. MOFs have a higher surface area (up to 2500 m²/g) than classical adsorbents (e.g. carbon, zeolite, meso-porous silica), this is considered one of the essential requirements in catalytic processes to ensure the presence of the largest possible number of active sites for adsorption of sulfur atoms. Future (MOF) materials

with extraordinarily high pore volume and specific surfaces with maximum pore size will be created using a variety of metals and linkers. MOFs are currently made from substantially all transition metals as well as some main group elements, such as magnesium (Mg), aluminium (Al), and beryllium (Be) [73, 82, 83]. Recently, nickel and cobalt nano-particles for the HDS process have been described and reported that Ni outperforms cobalt nano-particles in terms of efficiency [84]. Carbon nano-tubes were also evaluated as carriers for the HDS catalyst, and the results revealed that the sulfur content in the products decreased from 1126 mg/L to less than 10 mg/L [85]. Petzold et al. [86] Described nickel supported on zinc-oxide nano-wires as an HDS catalyst. In the beginning, the catalyst performed well in deep desulfurization, but then it was deactivated by coke after 16 hours. Brieva et al. [87] compared Y-Zeolite to numerous commercial MOF systems for removal of (T), (BT), (DBT), and (4-6-DMDBT) under various experimental settings. Li et al. [88] used five organometallic frameworks (MOF-5), (HKUST-1), (MIL-53 (Fe)), (MIL-53(Cr)), and (MIL-101(Cr)) to remove thiophene(T), benzothiophene(BT), and 4-6-Dimethyldibenzothiophene(4-6-DBT). Metal sites and a MOF structure are regarded as critical factors in adsorptive desulfurization. The impact of adsorbate-adsorbent interaction was examined using infrared spectra and temperature-programmed desorption. Chen et al. [89] employed density functional theory to analyze the contribution of each MOF fragment to adsorptive desulfurization. The greatest sulfur compound binding strength is found in the MOF with coordinatively unsaturated sites. Furthermore, when compared to Zn, Fe and Cu, MOF containing unsaturated Fe has the highest adsorption strength. Khan et al. [90] report on various applications of MOF in pollution control, in general, and desulfurization, in particular.

6.3. Graphene Nano-particle

Graphene is one of the fantastic materials that has attracted the scientific community due to its unique features and extensive range of technological applications in various sectors including the desulfurization process as shown in figure 9. Graphene is mainly composed of a repeat pattern of consecutive sheets layered on top of each other and held by Van der Waals forces, with a gap between one layer and the next of around 0.33 nano-meters. Each of these layers is two-dimensional, connected and layered in a hexagonal pattern and is one carbon atom thick. Figure 8 depicts the graphene structure and bonding. Graphene has a strong backbone structure (hexagonal geometry) due to carbon hybridising a structure with strong σ -bonds in the plane between carbon atoms and perpendicular π -orbitals, while out-of-plane π -orbitals interact with graphene sheets or other molecules (e.g., aromatic rings) [91, 92].

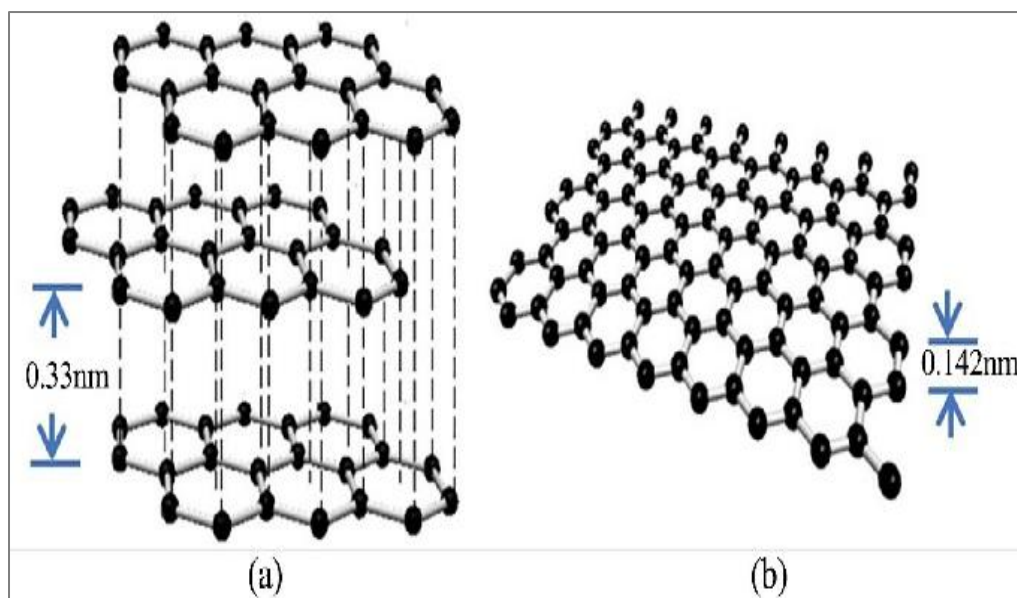


Figure 8: Schematic diagram of (a) Graphite and (b) Single layer of graphene from graphite [93].

Song et al. [94] investigated the adsorption of dibenzothiophene (DBT) on the graphene that is generated through grapheme oxide reduction. Graphite was initially oxidized using two ways to produce graphene oxide, which was then reduced to produce graphene. According to the data, one of the processes produced graphene oxide with a higher degree of oxidation and more interlayer space between the different layers. This specimen produced

graphene with fewer flaws, an enormous number of sp^2 carbon atoms, and a significantly higher specific surface area (853.9 m^2/g vs. 394.9 m^2/g for the other sample), resulting in a more efficient exfoliation. After batch adsorption of DBT from a model fuel, the sample's adsorption capacity was about double that of the faultier one (10.6 mgS/g vs. 5.5 mgS/g) (n-tetradecane).

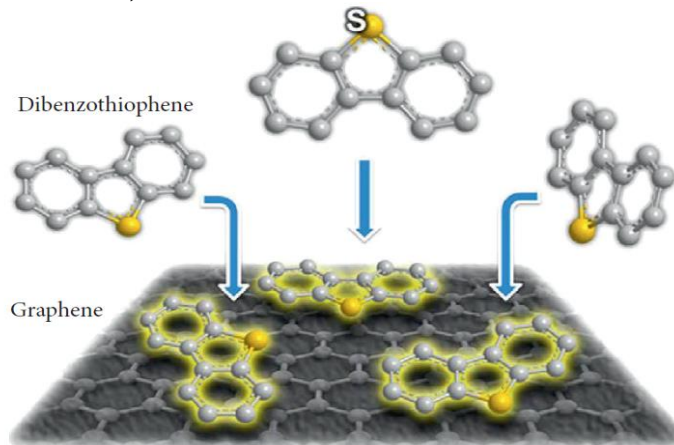


Figure 9: Adsorption of sulfur (DBT) on graphene via π -complexation [94].

6.4. Carbon Nano-tube CNTs

Carbon nano-tubes (CNTs) are cylindrical particles composed of single-layer sheets of carbon (graphene) coiled into a spiral. As illustrated in Figure 10, they can be single-layer (SWCNT) with a diameter of less than 1 nm or multi-walled (MWCNT) with a diameter of greater than 100 nm. They might be a few micrometers long or even several millimeters. The density of π -electrons of graphene layers' transitions from the concave inner surface to a convex outer surface due to the curvature, which leads to a potential difference of electrons on the walls of carbon nano-tubes [95]. This gives carbon nano-tubes interesting physicochemical properties that differ from other ordinary carbon materials. Several studies have been carried out to differentiate NPs within CNTs channels. [96–97]. Tawfik A. Saleh et al. [98] a report was conducted on the desulfurization of a common model fuel employing unique multi-walled carbon nano-tubes doped with titanium nano-particles (CNT/ TiO_2). The synthesized CNT/ TiO_2 nano-particles were shown to be efficient in eliminating sulfur compounds from a model fuel oil, according to preliminary data. A batch mode system was used to adsorb DBT, BT, and thiophene onto the resulting sorbents. In the beginning, these CNT/ TiO_2 nano-particles were able to remove around 45% of DBT, 55% of BT, and more than 65% of thiophene compounds from model fuels. The CNT/ TiO_2 nano-materials had a high level of activity when it came to interacting with organosulfur compounds. Because of their operational simplicity, high efficiency, and enormous capacity, we expect that these nano-materials as adsorbents will find key uses in the petroleum sector. Mohammed et al. [99] investigated the implanting of CoMo within the structure of multiwall carbon nano-tubes to create a nano-catalyst. Experiments with the nano-catalysts showed that they remove sulfur from fuel oil more effectively than traditional catalysts (CoMo/ Al_2O_3). As a result, there was a 10% increase in (HDS) over a conventional catalyst (73.5% maximum HDS). Table 1 lists the most prominent nano-sorbent materials employed by researchers in the adsorption procedure to remove different sulfur compounds.

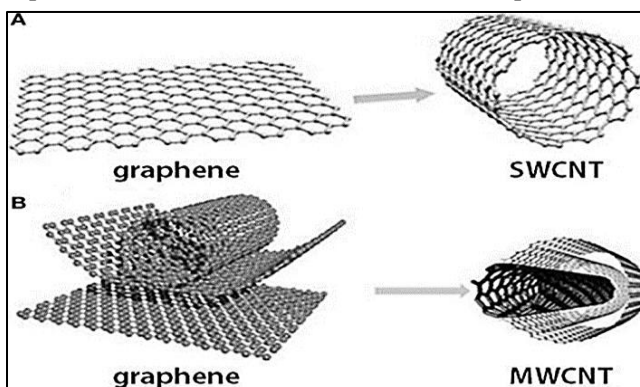


Figure 10: (A) single-walled, (B) multi-walled carbon nano-tubes [100].

Table 1: Nano-materials in the adsorption desulfurization process.

Nano-adsorbent	Sulfur components	Adsorption capacity	Ref.
Activated Carbon(AC)	Thiophene	1.28mg/g	[101]
	B-Thiophene	7.37mg/g	
	DB- Thiophene	11.54mg/g	
Graphene	Thiophene	2.72mg/g	[102]
AC	kerocen	3.65mg//g	[103]
Ce(IV)-Y	Kerocen (jet fuel)	2.30mg/g	[46]
AgNO ₃ /MCM-41	Thiophene	0.89mg/g	[101]
	B-Thiophene	1.28mg/g	
	DB- Thiophene	3.206mg/g	
Ag/ TiO _x - Al ₂ O ₃	Kerocen (jet fuel)	0.91mg/g	[104]
zeolite	4-6-DMDBT	1ml/g	[105]
(Activated carbon beads)	DBThiophene	8.2mgS/g	[106]
	Thiophene	88.2mgS/g	
SBA-15-Ni	Thiophene	0.43 mgS/g	[107]

7. Challenge in Nano-catalyst

Despite tremendous progress, there are still challenges in associating nano-material structures with catalytic features, which prohibits the design of catalytic active centres from the beginning. The major challenge is the creation of identical nano-structures. One more challenge is to understand the dynamic behaviour of catalyst nano-structures. Chemical catalysis is a dynamic process that takes place in the presence of a wide range of reagents and products at high temperatures and pressures (where applicable in the oil sector). NPs are supposed to be "sensitive" to such circumstances and to be able to endure considerable changes in composition, structure, and electrical state. These dynamic changes may to some extent resemble the observed changes in biostimulation systems. It is really important to associate the static structures of active centres with all of their dynamic structures. [53]. Table 2 summarizes several desulfurization procedures involving various nanocatalysts.

Table 2: Summary for catalysis desulfurization of the sulfur component.

Sulfur compound's	process	catalyst	removal (%)	Ref.
DBT (500 mg/L of S)	Adsorption desulfurization	Graphene Nano-particle	95.72	[108]
DBT (100 mg/L of S)	Adsorption desulfurization	nano-catalyst type Py/MOF-199	98.6	[109]
BT, DBT, and 4,6-DBT	Catalytic Oxidation desulfurization	Titania-silica nano-composite Ti-HMS/TS-1	98	[110]
Dibenzothiophene	Hydro- desulfurization	CoMo /activated carbon	98.8	[111]
T, BT, and DBT	Catalytic Oxidation desulfurization	Activated carbon supported phosphotungstic acid catalyst	90	[112]
Commercial kerosene	Adsorption desulfurization	montmorillonite clay (MMT)	76	[113]
BT (35 Mg/L of S)	Adsorption desulfurization	nano-catalyst type MOF-74(Ni) γ -Al ₂ O ₃	87.77	[114]
Dibenzothiophene (DBT) (Sulfur Concentration 5000 mg/L)	Hydro- desulfurization	CoMoP/ γ -Al ₂ O ₃	90	[115]
Commercial kerosene	Adsorption desulfurization	Tin impregnated activated charcoal (Sn-ACl)	99.4	[58]
benzothiophene	Hydro- desulfurization	NiMo/Al ₂ O ₃	89	[116]

8. Conclusions

The desulfurization of kerosene was investigated using several technologies include (HDS), (COSD), and (ASD). These methods have some advantages and drawbacks for deep desulfurization that depends on operation conditions, catalyst, and the characteristics of liquid fuels, such as their high boiling point, higher refractory sulfur contents, and the nature of refractory sulfur compounds. Nano-materials have the majority of the ideal catalyst qualities that improve the desulfurization process' efficiency, such as a large surface area, a large total pore volume, and a large micropore volume. However, it can be an excellent substrate for developing hybrids by combining them with other forms of adsorbents, such as organometallic complexes or metal oxide nano-particles, and increasing their effectiveness.

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Conflict of Interest

We certify that they have no affiliations with or involvement in any organization or entity with any financial interest or nonfinancial interest in the subject matter or materials discussed in the manuscript.

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