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Potential Role of Nanomaterial's In Oil and Gas Industry: Review on Downstream Stream Processing

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Abstract

Nanotechnology is the modern way of developing the products, which results the high efficiency of nanomaterial's use in the hydrocarbon recovery processes. Due to unique physico-chemical properties of nonmaterial have lead to their application in the field of petroleum processing industries, such as exploration, reservoir characterization, drilling, cementing, production and stimulation, enhanced oil recovery (EOR), refining and processing. In this review applications of nanotechnology through nano-catalysis in petro-refining processes, recent development of nonmaterial's were summarized. Finally, an outlook on the current challenges and some prospects for the future applications is also highlighted.

Keywords: Application; Material; Nanotechnology; Petroleum; Refining.

1. Introduction

The oil and gas industry will face significant technical challenges as readily exploitable resources are quickly reducing along with the increase in complexity of locating oil and gas reservoirs, eventually will result to rise in exploration cost in the long run. Furthermore, phenomenal emphasis on global energy usage and demand, an urgent attention for technological advancement in the sectors related to energy resources and production is required. Currently standard macro and micro material employed in petroleum and oil-refining sector has only yielded limited progress in tackling the difficulties. Nanotechnology is currently regarded as a game changer in the exploration and extraction of oil and gas resources, and is predicted to play a key role in the development of fossil-based energy technologies during the next 25 years. Crude oil consists of several saturated and unsaturated aliphatic and aromatic hydrocarbons and show variation in their compositions depending upon oil type. General composition of crude oil include paraffins - 15-60% , naphtthenes (30-60%) and aromatic hydrocarbons (3-30%) and asphatic (2-10%).The operational processes of oil and gas industry are categorized into three sections, namely , upstream , midstream and downstream . Downstream section deals with the refining of oil fractions into petroleum components such as gasoline, diesel and other feedstock required for petrochemical industries and purification of natural gas. The common products obtained from crude oil are gasoline, diesel, petrol, kerosene, liquefied petroleum gas, heating oil, fuel oils, lubricants, waxes, asphalt, and various petrochemicals. The main chemical process operational in downstream sector of oil and gas industry are Fluid Catalytic Cracking, hydrocracking, Catalytic Reforming and Isomerization Process (Fig.1)

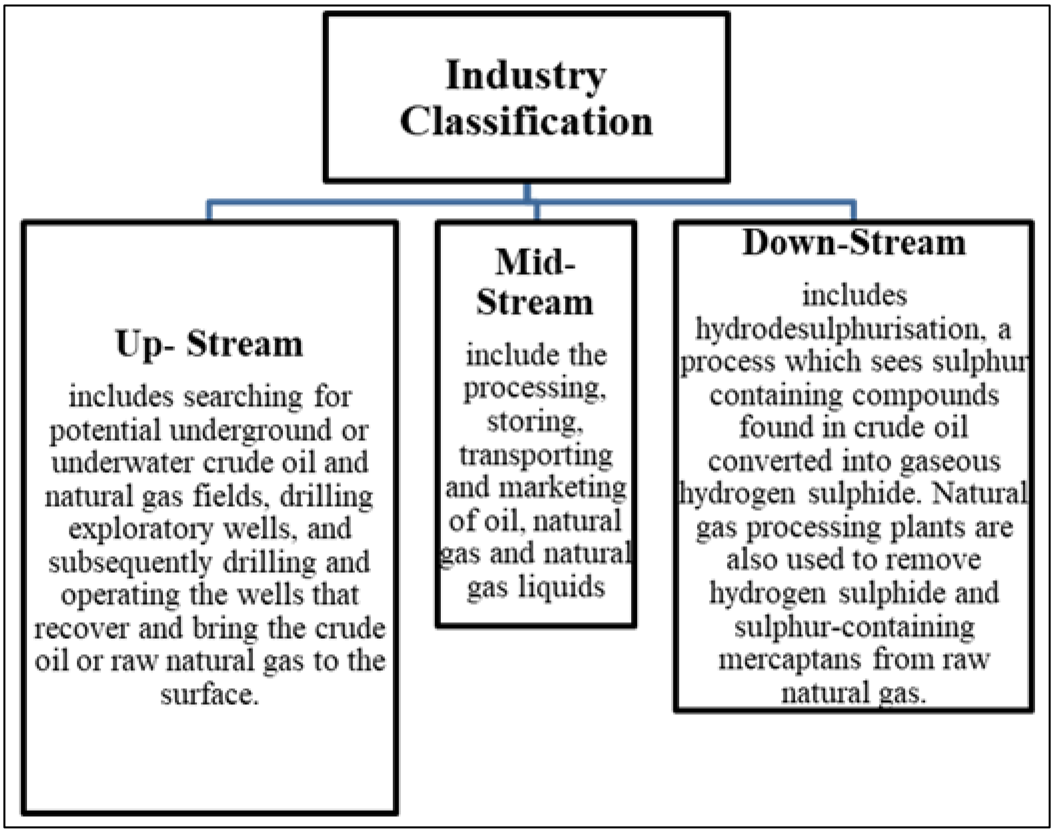

Fig-1. Petroleum Industry Classifications

Nanomaterials can contribute immensely by providing potential solutions for the challenges faced in the oil refining and petrochemical industry. The enhancementin variety of conversion processes was observed when nanometer-scale materials with superior propertiesare utilized [1]. The major advantages of using "nano-tech" in catalysis are due to increased exposed surface area for reaction, which reduces the possibility of formation of undesirable and side reactions. The use of nanoparticles as a proficient catalyst led to high activity, low deactivation, and minimal coke production to meet the growing needs of chemicals and fuels. In this chapter, we look at how nanotechnology may be used to improve the functionality and environmental compatibility of materials employed in the in petro-refining processes.

2. Nanomaterial's and Characteristics Features

Nanomaterials havingat least one dimension less than 100 nanometers exhibit distinctfeatures, which led to development of detectable traits possible only at nanoscale. Carbon materials, metals oxides, and zeolites are some of the examplesof nanomaterials used in industrial applications. Nanomaterials show distinct advantage of size dependency of properties and functions in comparison to their bulk counterpart (micro particles graeter than 1 µm). The physical and chemical properties of nanosized materials lies in between of atom size and its bulk substance. New and innovative functional features emerges at nanoscale dimensions such as colour change in terms of wavelength shift and emergence of new phases i.e. phase transition. Other important attributes are change in surface-to-volume ratio due to increase in the number of surface atoms which may be due to bulk size reduction or formation of open porous network within bulk materials during material growth [2, 3] (shown in Figure 2.). The nanoparticle size also has a impact on the chemical characteristics of nanomaterials and change in chemical potential is observable.

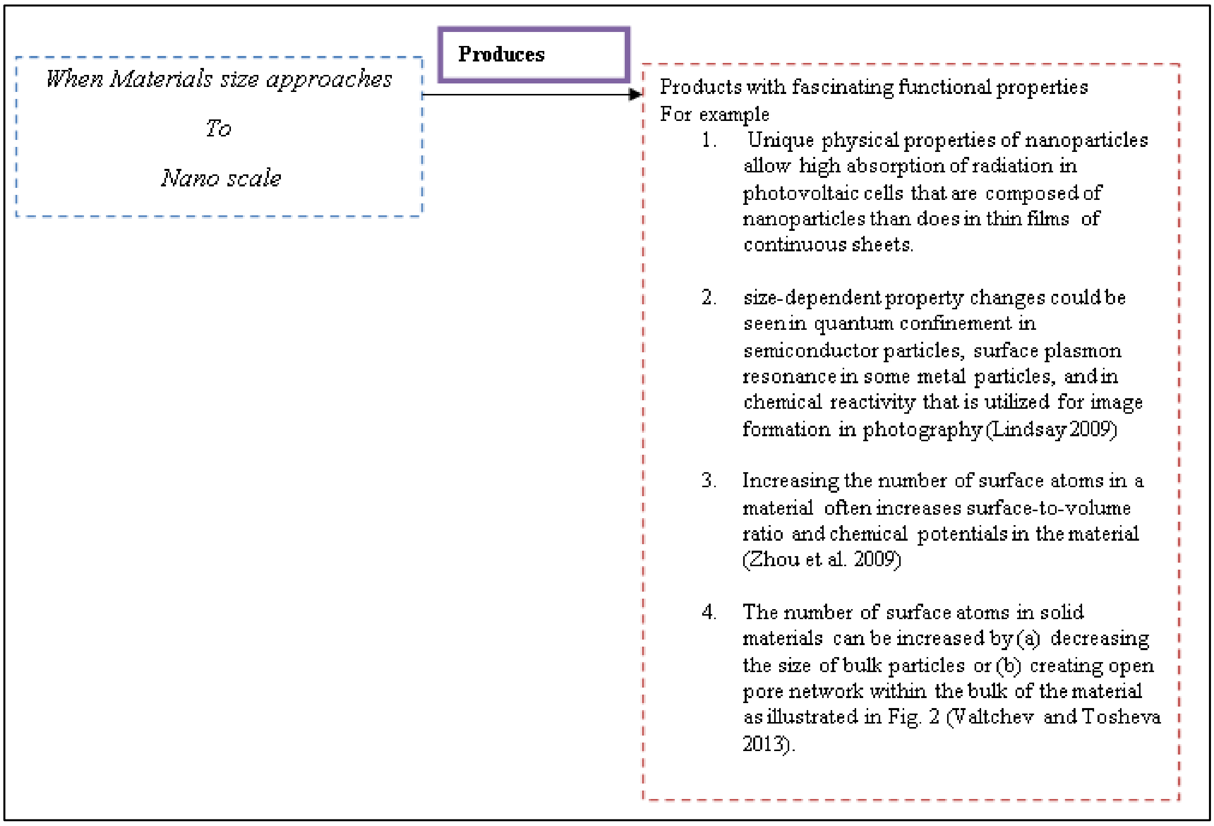

Fig-2. Emerging Features of Nanomaterial's

The fabrication of materials at the nanoscale needs careful design and selection of synthetic techniques/ methodologies, which entails the reaction, and assembly of reactants to form well controlled designed products. The synthesis may be performed either in the presence or absence of structure directing agents (SDA).The different synthetic approaches which involves the mechanical, thermal, or chemical processes are used to break down bulk materials into smaller particle size in the top down approach. The other prominent synthetic approach is bottom up strategy. The bottom up atrategy offers the advantage of better control over the partice sixe ; however the process is not economically effective due to the employment of costly precursors and surfactants. The top down approach has the drawback of non-uniformparticle size distribution. For example, Faujasite zeolite nanosheets are made by regulating the configuration with SDA and crystallization temperature, resulting in zeolite particle with interstitial pores between the nanosheet.

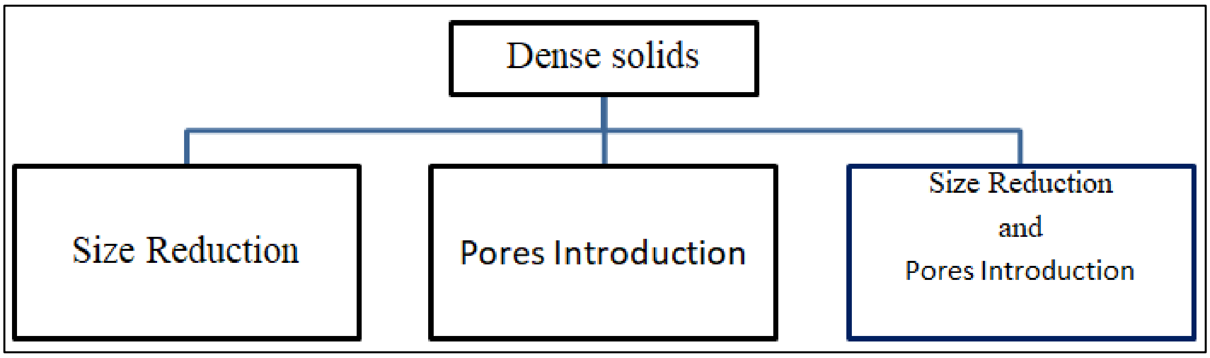

Fig-3. Ways to increase the Surface Area of Dense Solids

Thecatalytic application of nanomaterials depends upon their size , composition and surface properties, therefore utmost care must be taken during nonmaterial fabrication. The regulation of these properties and optimize surfacearea are crucial for their catalytic activity and stability for any desired catalytic application. When the dimension of a material is reduced, the surface area often increases due to the size shrinkage resulted in a larger proportion of the atoms found at the surface rather than in the bulk. The catalytic chemical reactions happen at the surface of materials, thus reactivity of nanomaterial is always more than a similar mass of bulk material. Additionally, materials that are inert in their bulk formmay become reactive at the nanoscaledue to energetically unstable state. Thus, nano materials are more reactive than bulk materials because more atoms at the surface are in energetically unstable states [2, 4].

3. Nanocatalysis

Nanoparticles plays a crucial role in petroleum petroleum refining by driving the processes involving both both homogenous and heterogenous catalysis. The surface structure and electrical characteristics of a catalyst shows size dependency and its performance is very sensitive to particle size. For example, increase in Ni particles influences the heat of adsorption for CO and the activation energy of CO dissociation, thus affecting thecatalytic performance of Ni nanoparticles in the Fischer-Tropsch synthesis of hydrocarbons from synthesis gas (shown in Figure 3). By shrinking the particle size of porous material to nano-dimensions, their applications in catalysis can be optimized [3].

Nanoporous materials have increased catalytic activity in diffusion-limited processes, and colloidal chemistry manipulation of nanocrystalline suspensions results in the fabrication of 2D and Small 3D building materials with structures designed for restoration processes. Nanocatalyst differs from conventional catalyst in terms of controlled design so as to extend the scale of much longer length than a single active site and formation of high-performance formulation at nanoscale level. Further, the use of nanocatalyst can reduce energy requirements in chemical processes, thus follows the principle of green chemical industry. Chemical process operating in the oil and gas industry at several stages, from upstream to midstream to downstream depends upon the usage of materials with distinct size- dependent properties [5]. Many catalysts used in the production of fuels and petrochemicals are of Nano range improve chemical processes [3].

3.1. Nano Zeolites in Catalytic Cracking

Cracking catalysts are usually crystalline aluminosilicate solid chemicals with strong acid properties to produce cuts of hydrocarbon carbon-carbon bond molecules. In contrast to heat dissipation, the use of powder catalysts opens up new cracks in the cracks and thereby by reducing the process capacity. Crystalline zeolites with well-defined 3D networks of micropores (1.2 nm) predominantly used as catalysts for cracking and play essential role in modern oil refining and petrochemical production. Zeolites are aluminosilicate minerals having well-defined pore linkage that depends on the structure. For more than 50 years, zeolites have made a significant contribution to the advancement of petroleum industry by contributing to the conversion of crude oil fragments into the most valuable and desirable products through the process known as Fluid Catalytic Cracking (FCC). Although zeolites have nanosized holes,however the particle size is commonly in the micrometre range. Thus the catalytic activity of zeolites is limited only at the external surface of zeolite. Only molecules of comparable or smaller size than the pore aperture can access the active sites due to these pore limitations. Catalytic reactions are thus limited to molecules with diameters less than the pore limitations. For instance, in catalytic cracking of gas oil, most of the hydrocarbon molecules are barred from zeolite pores and thus only the external surface of zeolite contributes to the gas oil conversion.

The usage of nanosized zeolite could circumvent this constraint because as the particle size reduces, the ratio of external to internal number of atoms increases, resulting in zeolite nanocrystals with a large external surface area and high surface activity. The increased surface area allows far more acidic spots to be exposed for catalytic reactions. Thus the advantages of use of nanosized zeolite nanoparticles are i) large external surface areas ii) high external surfaceacidity and activity. The cracking of higher hydrocarbon molecules is happened on the interface of zeolite–matrix component of the FCC catalysts and thus improved efficiency is attained [6, 7]. Further conversion and selectivity have shown to improve with decrease in crystallite size in cracking gas oil, [8]. Since the external surface of nanozeolites is expectedly higher and this type of surface is accessible, cracking of large hydrocarbon molecules on nanozeolites with high efficiency is possible. Because active sites are more accessible, catalytic performance improves. It has been proved that decreasing the zeolite crystallite size increases the conversion and selectivity of gas oil. Nanosized zeolites have stronger activity, reduced coking activity, and a longer life in many processes than micron-sized zeolites [9]. Out of 230 species of zeolites, the most common ones being used in petroleum and petroleum refining industries are Zeolite Y and ZSM-5 with FAU and MFi topologies. These zeolites must contain nano-pore to allowing the functions of sieving cells. The appropriate nano-pore diameters (0.74-1.2 nm in zeolites Y and 0.54-1.0 nm is ZSM-5) allow the screening out heavier hydrocarbon molecules are and only molecules with a diameter less than or equal to their pore size to pass through the nanosheets Their remarkable architecture along with functional characteristic made them suitable for industrial operations [10].

In the FCC process, NaYzeolite crystals with a diameter ranging from 60 nm to 0.65 m were converted to a flexible electric oil converter. The catalyst with the smallest particles has improved in terms of function and selection of petrol and small-scale flour (LCO). This increased choice is due to the resistance to the reduced zeolite distribution of fossil fuels and synthetic fuels. Hydrocarbon conversion can be greatly enhanced by nanozeolite. created a variety of zeolite Y nanocrystals and tested its experimental function in a standard oil-cracking test. There is a link between the selection of fuel and the size of the zeolite particles in the conversion of FCC feedstock [6]. This functional activity of the zeolite catalyst can be explained by the breakdown of the FCC feed in the outer part of the zeolite crystals: FCC-100 FCC40 FCC-25. By reducing the size of the crystallites, the internal properties of the catalyst can be altered. Nanosized ZSM-2 (100 nm) was developed [11] has increased acidity, surface area, and structural stability, making it ideal for catalytic use. In bio-oil conversion, nanoporous aluminosilicate (MMZUSY) found in USY zeolite shows greater thermal stability and the availability of oil molecules. Compared with MCM-41, MMZUSY showed higher imaging activity and selectivity due to increased acidity. The fragmentation activity of FAU nanozeolites (zeolite Y) and MFI type (ZSM-5) on the outer surface was tested in 1,3,5-triisopropylbenzene conversion and was compared with standard crystals of zeolite Y and ZSM-5 used as samples reliable [7].

3.2. Nanomaterials as Catalyst Support

Advances in the materials processing led to the development of new methods for the production of very small catalyst particles for various purposes. These catalysts are required to be fixed or supported on a porous base for most applications. In practice, fixed catalysts designed are more stable than their mass counterparts because of the greater surface energy and increases the efficiency.

Among the most widely used support materials for catalyst fabrication, alumina and silica are commonly used due to low cost and outstanding physical properties as catalysts sponsors [12]. In the industrial scale, alumina is widely used as a resource for several iron ore and sulphide catalysts. The high-quality alumina support based catalysts (having metal - platinum, palladium, or metal sulphides as active phase) are used for operations involving hydrogenation reactions at low temperatures (below 500C). Aluminas reinforced with silica or alkali, alkaline earth metals or rare earth metal cations (K +, Ca2 +, La3 +, etc.) are widely used for reactions requiring medium temperature process. For endothermic processes such as vapor conversion or partial oxidation, platinum or rhodium-based nano catalysts are used. Silica-based catalysts are also widely used due to the robustness of machinery and their heat [12, 13].

The metal nanooxides such as Al_2O_3, anatase TiO_2, and tetragonal ZrO_2 are used as support and also provide an effective way to control the structure and electrical properties of supported nanocatalysts without affecting their structure. The active metal's particle size reduction provides a significant benefit in terms of energy cost reduction. Au nanoparticles with dimensions smaller than 10 nm are frequently employed in a variety of applications, including catalysis. In catalysis, selective oxidation of ethanol in oxygen catalysed by SiO_2 supported Au has higher activity at lower temperatures than bulk Au. Aside from improved catalytic activity, this behaviour indicates the energy conservation that comes with smaller particle size catalyst. The size of Co particles is important in determining their selective performance [14].

Nnaomaterials in Catalytic cracking of Naptha :

The production of specific lighter olefins such as ethylene and propylene, which serves as basic raw materials for petrochemical industries, is an important task. The ligther olefin is produced from naptha either by thermal or catalytic cracking. Thermal cracking of naptha is an energy intensive process consuming almost 30% of the total enegy consumed for petrochemical process and producing relatively low percentage 25% and 13% of ethylene and propylene.

The catalytic cracking of naptha yield high propylene /ethylene ratio even at low temperature thereby leading not only cost reduction but also selective better yield of propylene. Zeolite is extensively employed for catalytic cracking of naptha due to following characteristics

1. Strong solid acid catalyst
2. High surface area
3. Existence of micropores and nanospaces of dimensions compatible with molecular size of lighter hydrocarbons
4. It can sieve the ligther hydrocarbons,act as promising molecular sieves
5. It can be used as shape selective catalyst for different hydrocarbon processes.

   Despite many of its advantages, the main limitations of employing Zeolites as specific catalyst is its crystal size, which impairs with life time of catalysts leading to instability. The high diffusion of reaction reactants and products in the mesopores or plugging of pores with solid carbon particles led to the poising of catalyst.

   As evident from discussion, zeolite catalyst framework is appropriate for the petrochemical processes if maneuvering of the zeolities external surface area and thereby controlling the diffusion resistance improvement in catalytic activity and life time can be attained. This has been made possible by employing nanozeolites .

   Ref. Kinetics of n-hexane cracking over ZSM-5 zeolites – Effect of crystal size on effectiveness factor and catalyst lifetime Hiroki Konno, Takuya Okamura, Takahito Kawahara, Yuta Nakasaka, Teruoki Tago ⇑ , Takao Masuda and inside refernces from this.

3.3. Nanomaterials in Fisher-Tropsch Synthesis Process

Fischer-Tropsch synthesis process led to conversion of coal, biomass and natural gas into hydrocarbon derivatives. However, the process offers less selectivity toward lower olefins. Lower olefins having two to four carbon atoms constitutes the important raw materials in chemical industries for production of wide range of products such as polymers , solvents , drugs etc. The environmental issues and to shift the dependency from crude oil , alternative source of fuels, biomass is extensively explored by the researchers for production of lower hydrocarbons. Fischer Tropsch to olefins (FTO) provides a direct route for transforming syngas to light olefins, without intermediate steps using catalysts. Among the various catalyst, bulk iron FT catalysts alone or modified with promoters offers the greater selectivity (upto 70wt%) for lower olefins (8, 9,12). The advantages of Fe catalyst zed process are i) direct conversion of syngas to olefins ii) decreases the formation of methane iii) does not require the maintenance of H2-CO ratio .

However the disadvantages for the use of bulk iron are

i) Mechanically stablility of catalyst at high temperature
ii) Blockage of the active sites due deposition of carbon
iii) Plugging of catalyst bed etc.

Supported Iron nanoparticles as catalysts can also the issue of mechanical staboility and provide active surface for reactivity. Numerous supports for iron-based FTO catalysts such as alumina (15, 16) , zeolites (18) and carbonaceous materials (20, 21) etc . has been employed . To overcome the low activity and mechanical stability problems, we explored the use of support materials weakly interactive toward iron. As a working hypothesis, we posited that these inert supports would impart mechanical stability to the iron nanoparticles without inhibiting their activation. Inert supports based on nanostructured carbon materials such as carbon nanofibers (CNF) and carbon nanotubes (24, 25), provides promising results in terms of higher reactivity and stability owing to their high specific surface area, inertness, and good mechanical strength

Besides the above-mentioned applications, catalysts play crucial role in isomerization and hydrocracking processes. The catalyst activity can beenhanced in the presence of cocatalyst or metal promoted catalytic response. For instance, a bifunctional catalyst consists of the uniform sized Co nanoparticles and mesoporous H-ZSM-5 was found to be highly efficient hydrogenation and hydrocracking/isomerization process. The better efficiency was observed due to the cooperative interplay of the Co sites and the acid sites on the zeolites.

Catalytic cracking of n-hexane over ZSM-5 zeolite catalysts was examined at a reaction temperature of 823–923 K under atmospheric pressure. The reaction rate constant and the activation energies of n-hexane cracking over ZSM-5 zeolites with different crystal sizes and Si/Al ratios were evaluated. Compared with the macro-zeolite, the nano-zeolites exhibited high n-hexane conversion with stable activity for 50 h. This is because the cracking reaction with the nano-zeolites proceeded under reaction-limiting conditions, whereas the reaction with the macro-zeolite proceeded under transition conditions. Moreover, the large external surface area and low diffusion resistance of the nano-zeolites reduce the effect of pore plugging due to coke deposition. As a result, the application of nano-zeolite in the catalytic cracking of n-hexane was effective in the stabilization of the catalytic activity.

3.4. Desulfurization of Petroleum

Petroleum reductions are widely used to reduce the sulfur content of pure petroleum products to less than 10 percent as per stricter regulations imposed by various environmental groups around the world on the release of toxic gases from the environment because of fuel exploitation [15]. The removal of sulfur compounds from oil is another big challenge, which can be addressed by application of various nanomaterial developed and evaluated for such applications.The metal catalysts such as cobalt and nickel-based nano catalyst are used to remove sulfur from petroleum and petroleum products.

4. Overview and Future Prospectus

The relationship between nanoscience / nanotechnology and catalysis provides great opportunities for improvements in fuel consumption. The use of nanoporous materials as additives and as active ingredients and metallic nanoparticles for catalytes break down various petroleum refining processes. The great advantages of nanoscale materials have over their parallel micron counterparts is due to their size-dependent properties in the formation of nanoparticles suitable for efficient operation requiring carefully designed and controlled experiments. The development of several factors makes them prefer to bet. Factors that make them suitable for the manufacture of fuel include a larger area than the average volume due to the smaller particle size, and the heat resistance and durability. Although the physical characteristics of nanoparticles such as phase, composition or behavior, can be influenced by the method of preparation and the environment in which the nanoparticles are placed to the level of these substances in particle materials can also depend on size and therefore can be controlled. The natural stability of nanoparticle catalysts and their bifunctional catalysis potential provides many future opportunities for many applications. Catalytic applications in renewable fuels, for example, nanotechnology are set to change the world and continue to improve future exploration and exploitation of crude oil. Low power consumption and long system life expectancy is expected. As well as reducing the amount of material used and reusing nanomaterials it will provide more in the future, using environmentally friendly solutions.

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