

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/284901229>

# Carbon-Based Nanomaterials for Desulfurization: Classification, Preparation, and Evaluation

Chapter · October 2015

DOI: 10.4018/978-1-4666-9545-0.ch005

---

CITATIONS

6

---

READS

2,417

Some of the authors of this publication are also working on these related projects:



Enhancing the Solubility of a Drug using Novel Formulations [View project](#)



Novel Isotope Labeling Strategy for NMR-Based Structure Determination [View project](#)

# Applying Nanotechnology to the Desulfurization Process in Petroleum Engineering

Tawfik A. Saleh

*Department of Chemistry, King Fahd University of Petroleum and Minerals,  
Saudi Arabia*

A volume in the Advances in Chemical and  
Materials Engineering (ACME) Book Series



An Imprint of IGI Global

Published in the United States of America by  
Engineering Science Reference (an imprint of IGI Global)  
701 E. Chocolate Avenue  
Hershey PA, USA 17033  
Tel: 717-533-8845  
Fax: 717-533-8661  
E-mail: [cust@igi-global.com](mailto:cust@igi-global.com)  
Web site: <http://www.igi-global.com>

Copyright © 2016 by IGI Global. All rights reserved. No part of this publication may be reproduced, stored or distributed in any form or by any means, electronic or mechanical, including photocopying, without written permission from the publisher. Product or company names used in this set are for identification purposes only. Inclusion of the names of the products or companies does not indicate a claim of ownership by IGI Global of the trademark or registered trademark.

Library of Congress Cataloging-in-Publication Data

Applying nanotechnology to the desulfurization process in petroleum engineering / Tawfik A. Saleh, editor.  
pages cm

Includes bibliographical references and index.

ISBN 978-1-4666-9545-0 (hardcover) -- ISBN 978-1-4666-9546-7 (ebook) 1. Petroleum--Refining--Desulfurization--Materials. 2. Petroleum--Refining--Desulfurization--Technique. 3. Nanostructured materials. I. Saleh, Tawfik A., editor. TP690.45.A66 2016  
665.5'3--dc23

2015033323

This book is published in the IGI Global book series Advances in Chemical and Materials Engineering (ACME) (ISSN: 2327-5448; eISSN: 2327-5456)

British Cataloguing in Publication Data

A Cataloguing in Publication record for this book is available from the British Library.

All work contributed to this book is new, previously-unpublished material. The views expressed in this book are those of the authors, but not necessarily of the publisher.

For electronic access to this publication, please contact: [eresources@igi-global.com](mailto:eresources@igi-global.com).

## Chapter 5

# Carbon-Based Nanomaterials for Desulfurization: Classification, Preparation, and Evaluation

**Tawfik A. Saleh**

*King Fahd University of Petroleum and  
Minerals, Saudi Arabia*

**Gaddafi Ibrahim Danmaliki**

*King Fahd University of Petroleum and  
Minerals, Saudi Arabia*

**Taye Damola Shuaib**

*King Fahd University of Petroleum and  
Minerals, Saudi Arabia*

**Mohammed A. Al-Daous**

*Saudi Aramco, Saudi Arabia*

### ABSTRACT

*The special interest in ultra-low sulfur diesel (ULSD) is informed by the need to comply with the strict government policy on low sulfur content of transportation fuels. Better knowledge of different factors that concern deep desulfurization of fuels is important to achieve ultra-low sulfur fuels and cheaper way of producing ULSD. Both the capital and operating cost of the adsorptive desulfurization process is cheaper compare to the conventional hydroprocessing. The need to produce more volume of fuel such as diesel with very low sulfur content from low grade feed stocks like heavy oil and light cycle oil (LCO) in order to meet up with the global demand for sulfur-free fuels is pertinent. Several on-going researches are pointing to the use of adsorbents for removal of sulfur compounds from the hydrocarbon refining stream. In this chapter, varieties of carbon nanomaterials suitable for adsorptive desulfurization are discussed. The approach is feasible for commercial applications with any adsorbent of an adequate lifetime of activity as well as high capacity.*

### 1. INTRODUCTION

Desulfurization is a vital unit operation in petroleum refining since the combustion products of sulfur compounds are the main reason for acid rain and environmental pollution. In addition, sulfur is also a catalyst poison during industrial processes. Compounds with sulfur are removed catalytically at high temperature and pressure. Desulfurization is gaining a lot of attention and efforts have been channeled towards investigating several methods that are effective and economically viable. The attention is warranted

DOI: 10.4018/978-1-4666-9545-0.ch005

by stricter environmental regulations on the amount of sulfur that should be present in transportation fuels (Song, 2003; Yang et al., 2004). Sulfur limit (mass percent) of 0.015, 0.035, and 0.2 for gasoline, diesel fuel and light fuel oil, respectively has been set. A new and more stringent limit of 0.003-0.005 mass percent (30-50 ppm) is imminent for transportation fuels in Europe and United States of America (Song, 2003; State Announcer, 2001; Babich and Monlijn, 2003). It's worthy to note also that; desulfurization processes have found applications in converting used tires and shale oil to fuel oils. Using calcium oxide in binding up sulfur oxide in emissions has been achieved for stationary applications in the desulfurization of non-transportation fuels, but the use of the harmful compounds still a challenge (Svobodal et al., 1994). Therefore, the need to innovate effective technologies for desulfurization processes is paramount.

Several methods of desulfurization processes have been investigated for many years. The need to achieve a lower level of sulfur in fuel oils has also called for different innovative ways of achieving deep desulfurization where the synergy of methods yielding better results (Agarwal and Sharma, 2010; Sundaraman et al., 2009). Hydrodesulfurization (HDS) is a popular process, but there is wide variation in reactivity of sulfur-containing heterocyclic compounds. Alkyl-substituted derivatives of dibenzothiophene like 4-methyldibenzothiophene and 4, 6-dimethyldibenzothiophene from fuel oils have been reported to be relatively unreactive towards hydroprocessing (Gate and Tropsoe, 1997). In order to achieve deep-desulfurization and take care of attending challenges of hydrodesulfurization that include high hydrogen consumption, energy (heat) cost, catalyst volume etc. Many other methods are combined with HDS for better results (Rana et al., 2007). In recent years, efforts are being directed to other methods, including; adsorptive desulfurization, oxidative desulfurization where different catalysts are used (Kumar et al., 2012) extractive desulfurization involving ionic liquids, photochemical activation, bio-desulfurization, ultrasonic-desulfurization, microwave desulfurization and electrochemical approach (Bhatia and Sharma, 2006; Lam et al., 2012).

Adsorptive desulfurization where adsorbents are used to remove sulfur-containing compounds in fuel oils is holding future promise of ultra-clean sulfur-free fuel oils. Adsorption processes can be performed at ambient temperature and pressure, thus saving a lot of energy as compared to other methods of desulfurization (Seredych et al., 2009). Therefore, intensive research is ongoing to produce new adsorbents with great emphasis on good selectivity, high capacity for adsorption and regeneration of the adsorbents with special attention to the mechanism of adsorption (Yang et al., 2007). Various materials have been reported to be good adsorbents for different adsorption processes. These materials include; different types of zeolites and metal-impregnated zeolites such as MCM-22 zeolites (Delitata et al., 2008), MCM-41 (lanthanum loaded, sorbents for diesel fuel) (Subhan et al., 2012), Y-zeolites with exchanged cation (NaY) and carbon nanotubes (CNT) as a template, Ag- and Cu-beta zeolites among others. A deep desulfurization method was presented by Daimler-Chrysler AG (2000) where the adsorption process is used for engine fuel with  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  (with metal additives) as adsorption materials. Dibenzothiophene (DBT) and 4, 6-dimethyldibenzothiophene (4, 6-DMDBT) can also be removed from diesel by using mesoporous carbon synthesized from silica HMS (template) and phenolic resins (sources of carbon) (Zhou et al., 2009). Due to high thermal stability, large surface area and well-arranged mesoporous structure (Arbia and Parvin, 2011) of carbon molecular sieves (CMK-1, 3 and 5), they have been implicated as promising adsorbents of DBT in petroleum fuels.

The following sections will highlight a general classification of carbon materials based on their constituents; discuss major techniques commonly used in their preparation and evaluation of these valuable materials towards desulfurization.

## 2. CLASSIFICATION OF CARBON-BASED MATERIALS

This section discusses carbon-based materials and their classification based on constituents (Figure 1).

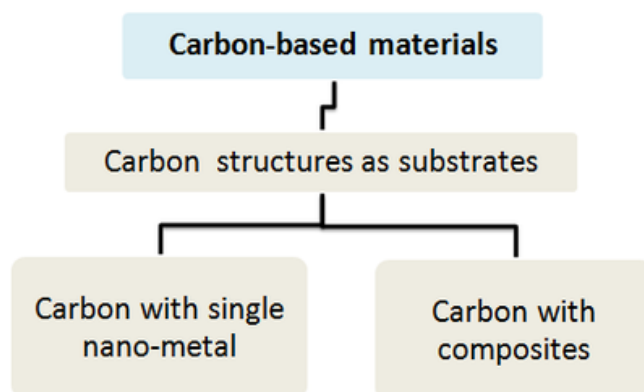
### 2.1 Carbon Structures as Substrates

Structure indeed determines properties. Different allotropes of low dimension can be formed from carbon, such as; graphene, CNT and C-60. The superiority in properties exhibited by CNT among other 1-D nanomaterials can be traced to its special stereogenic structure. Several attentions have been paid to CNTs over the past two decades; this is due to nothing but unique mechanical, thermal, electrical properties among other key applications in many fields of science and technology (De Volder, et al., 2013; McEuen, et al. 2002; Terrones, 2003; Zhang, 2013).

Over the years, carbon has been used as catalyst support employed for different applications in the chemical industry owing to its fascinating surface nature. The orientation of graphene layers can be varied with respect to the axes of carbon nanofibres (CNFs) giving different morphologies, which make available different pores for catalysts' nanoparticles (Salernitano et al., 2014). Carbon paper substrate with 3-D fibre network is appropriate in fuel cells with Silicon-Carbon composite deposited alongside the fibre network on the electrode (Matsiu et al., 2013). Carbon blacks and typically, acetylene black, have been deeply investigated electrochemically (Kinoshita and Bett, 1973) and gained applications in many areas, like catalysis, energy storage and fuel cell technology (Zhang, et al., 2010). An effective interaction (oxidation-reduction active species) is owned to a large surface area of carbon (particle size 1-50 nm, commercially available).

Although carbon black is not well defined structurally like CNT, graphene materials or nano-onions but their activities in carbon-based nano-sensor, polymer nanocomposites (selective shape sensing), fuel cell and energy storage are very excellent (Iijima, 1991; Molina-Ontoria, et al., 2013; Novoselov, et al., 2014; Loo, et al., 2013; Li, 2009; Blanco-Lopez, et al., 2004). Correct choice of nanocarbon substrate is very vital in electrocatalysis and fuel cells, the effects of this have been critically reviewed (Dribinskii, et al., 1989). Pt-carbon nanomaterial composites have found application in fuel cells that is characterized by CO<sub>2</sub> reduction (Perathoner, et al., 2007). With adequate optimization for stable operational conditions, carbon blacks give allowance for gas flow into catalysts' reactive layers.

Figure 1. Classification of carbon-based materials



## **2.2 Carbon with Single Nano-Metal**

Carbon possesses ordered structure which provides its framework with good porosity. However, their uses are limited due to poor solubility, thus limited functionalized nanocomposites of metals and CNTs can be achieved (Ebbesen et al., 1996). However, the increasing development of CNTs chemistry makes possible the preparation of hybrid materials (metals and CNT) with enhanced performance (Ding et al., 2012; Li et al., 2011). These hybrid materials can function as chemical sensors due to their high conductive (electrical) power and selective chemical nature. Another vital property they possess is reasonably large surface area, which provide them with good catalyst, sites in reaction catalysis (Ding et al., 2012). Nanomaterials of low dimension can now be used for electronic applications, chemical sensors, adsorption (desulfurization) e.t.c (Geim AK, 2009). In the same manner, graphene supported metal nanoparticles also performs well (Huang et al., 2012; Bai and Shen, 2012).

Metal-carbon interactions play critical roles in catalytically growing carbon nanotubes and graphene via CVD as well as in controlling the structures of these carbon allotropes and, consequently, have been intensively investigated in order to elucidate the catalytic mechanisms (Jourdain and Bichara, 2013; Mattevi, 2011; Li, 2010; Ding, 2008; Edwards, 2013; Seah, 2014; Cheng and Guo, 2002). Fe and Cu are two metal systems exhibiting distinct interactions with carbon (Naidich, 1981). With partially filled 3d-orbitals, Fe exhibits a high affinity for carbon. Carbon has a finite solubility in Fe at high temperatures (0.022% carbon by weight in  $\alpha$ -Fe at 727 °C and 2.14% carbon by weight in  $\gamma$ -Fe at 1147 °C) and forms metastable iron carbide ( $\text{Fe}_3\text{C}$ , 6.67% carbon by weight) with Fe (Jourdain and Bichara, 2013; Mattevi, 2011).

Due to its strong interactions with carbon, Fe was among the first catalysts and has been most intensively used for CVD growth of single-wall carbon nanotubes (SWCNTs). In contrast, with completely filled d-orbitals, Cu displays a low affinity for carbon. The carbon solubility in Cu is much lower than in Fe (~ 0.008% carbon in Cu by weight at 1085 °C) and there is no carbide formation (Jourdain and Bichara, 2013; Mattevi, 2011). Due to the weak Cu-C interactions, Cu was once considered unsuitable for CVD growth of carbon nanotubes (Deck and Vecchio, 2006). However, this notion did not stop the exploration of using Cu as the catalyst. In fact, it has been demonstrated that Cu can catalyze the growth of SWCNTs (Yoshida et al., 2009; Zhou, 2006) and, furthermore, it is a better catalyst for developing SWCNT system using quartz and silicon as substrates (Li et al., 2010 and Cui et al., 2010). In terms of the metal-catalyzed CVD growth of graphene, the different interactions with carbon between Fe and Cu result in the formation of few-layer graphene (FLG) on Fe foil (Xue et al., 2011) and monolayer graphene on Cu foil (Li et al., 2009). With the formation of methane, carbon hydrogenation reverses the reaction for CVD growth of carbon nanotubes and graphene using methane as the carbon source. It was demonstrated that Fe is an active catalyst in producing methane and in etching channels in graphite. Though an initial study showed that Cu was inactive in catalyzing the hydrogenation of graphite, Cu was later found to be active in catalytic etching channels in graphite (Baker, 1981 and 1995).

Metals of transition series are good options for growing graphene or CNTs. The metal-carbon system can be built by performing the growth and contacting in a single step with the same metal. However, a pressing challenge here is oxide layer formation on exposure of nanoparticles of metal to air as it tarnishes and form oxide coating. The formation of the oxide coatings is largely due to large surface-volume ratio, which translates to high oxidation process. The oxidation process at the metal surface can, however, is

prevented in the procedure (Geim AK, 2009). Scanning electron microscope (SEM) reveals the porosity of carbons is paramount to their adsorptive properties. Figure 2 shows SEM images of different carbon structures such as activated carbon (AC), CNT and graphene.

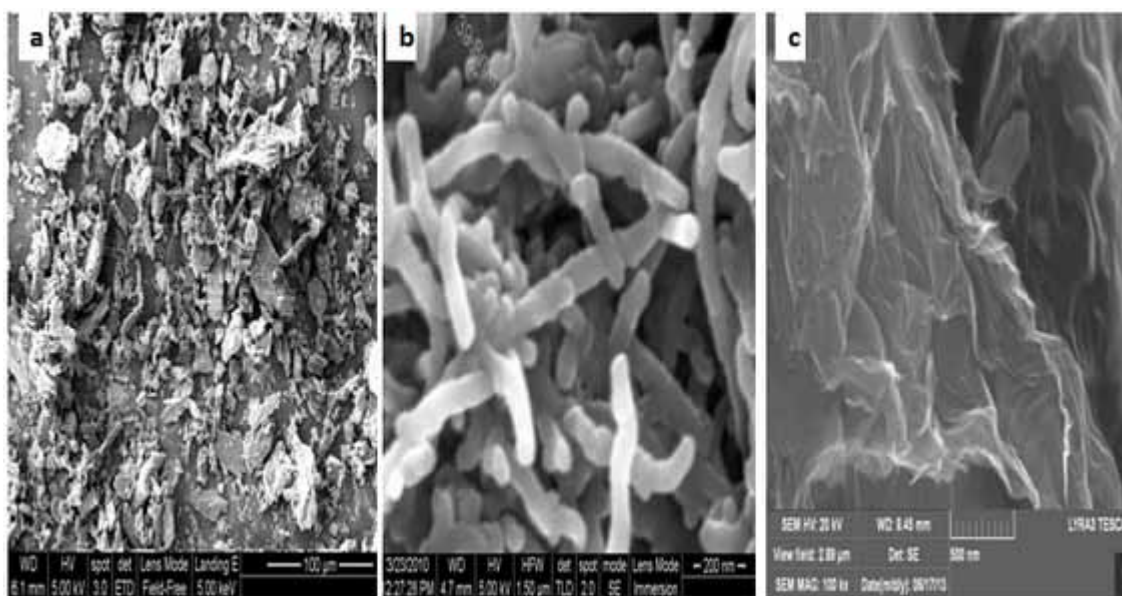
### 2.3 Carbon-Based Composites

The good surface chemistry, stable structure and very large surface area are factors enabling the fine surface templating property of graphitic supports (carbon nanospheres (CNSs), CNT, and graphene) and their decoration with metal nanoparticles (Iwamoto and Grimblot, 1997). The composites formed show **enhanced or even synergistic activity in their** applications (Salem and Hamid, 1997). The surface chemistry of the composites, however, is not fully established and still open to further studies (Nagai et al., 2000).

Carbon nanomaterial composites made by decorating carbon (graphene, carbon nanospheres, and carbon nanotubes) with transition metals (oxides or salts) are receiving great attention. Carbon-supported metal nanoparticles (MNPs) for example; cobalt, iron, or nickel based nanoparticles (CoOx–CoP/C or FeOx–CoP/C) have been confirmed to be catalytically active for oxygen reduction reaction (ORR); this is due to the nature of the transition metals oxide nanoparticles (Stephanie, et al., 2010). The confirmation of this great activity is shown in the less activity of cobalt porphyrin (CoP/C) when it is adsorbed on unmodified carbon. Sometimes a synergistic activity is observed (Salem, 1997).

In the investigation of the potency of activated carbon materials for desulfurization and denitrogenation gas oils, MAXSORB-II adsorbent, is an effective adsorbent for organosulfur compounds' adsorption at ambient temperature (Mochida et al, 2004a and 2003c). This material can be prepared by activating carbon prepared from petroleum coke with KOH. Oxidizing agents as  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  were also used

Figure 2. SEM images of nano-structured carbons of AC (a), CNT (b) and graphene (c)





to further enhance the adsorptive power of commercially available activated carbon, which is then heat-treated (Mochida et al., 2004b, 2003d). These oxidizing agents aid the release of CO (600-800 °C) at the carbon surface, which thus enhances the absorption power.

### **3. PREPARATION OF CARBON STRUCTURES**

There are three main techniques of preparing carbon nanomaterials such as CNT, CNS, CNF, graphene etc. (Iijima, 1991; Yudasaka et al., 1997; Li et al., 1996). These techniques are listed in Figure 3. Other techniques that are commercially less developed compare to the above-mentioned three which involve the use of flame, solar, electrolysis in their syntheses (Yuan et al., 2001; Hsu et al., 1996; Laplaze et al., 1998).

In the arc discharge technique (Figure 4), with a space of less than 1 mm between graphite electrodes, a direct current is passed under inert environment argon at a low pressure. An illustration of arc discharge technique is depicted in Figure 3. The carbon anode vaporizes on generation of plasma of very high temperature on the application of current and the carbon material is deposited alongside other by-products of carbon at the cathode (Popov et al., 2004; Journet et al., 1998). The production of MWNTs with diameters ranging from 2 to 20 nm and micrometer-scaled length can be achieved (Ebbesen and Ajayan, 1992). Similarly, SWNTs of above 70% yield and diameter of close to 1.4 nm can be prepared (Journet et al., 1997).

In the laser ablation technique, the principle is not so different from the arc discharge. The heating is done in a furnace with the aid of pulsed laser source under inert surrounding. In this technique, high temperature carbon vapor is generated from the surface of the graphite as illustrated in the Figure 5 (Journet et al., 1997). The carbon vapor is transported by the flowing helium or argon and then collected on copper-collector as illustrated in Figure 3.

These first two techniques produce high quality carbon nanomaterials in a large amount. However, some shortcomings have been identified; the reliance on high temperature graphitic surface evaporation

*Figure 3. Techniques used in preparation of carbon structures*

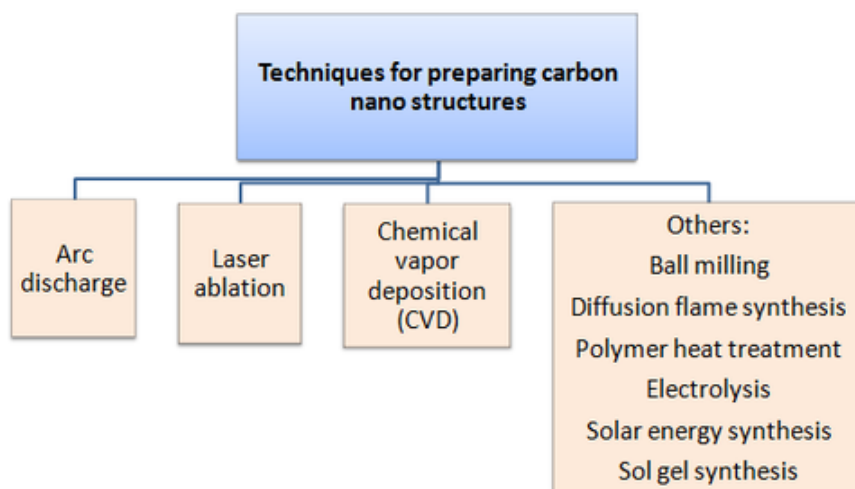


Figure 4. Schematic representation of arc discharge technique for synthesis of carbon nanomaterials

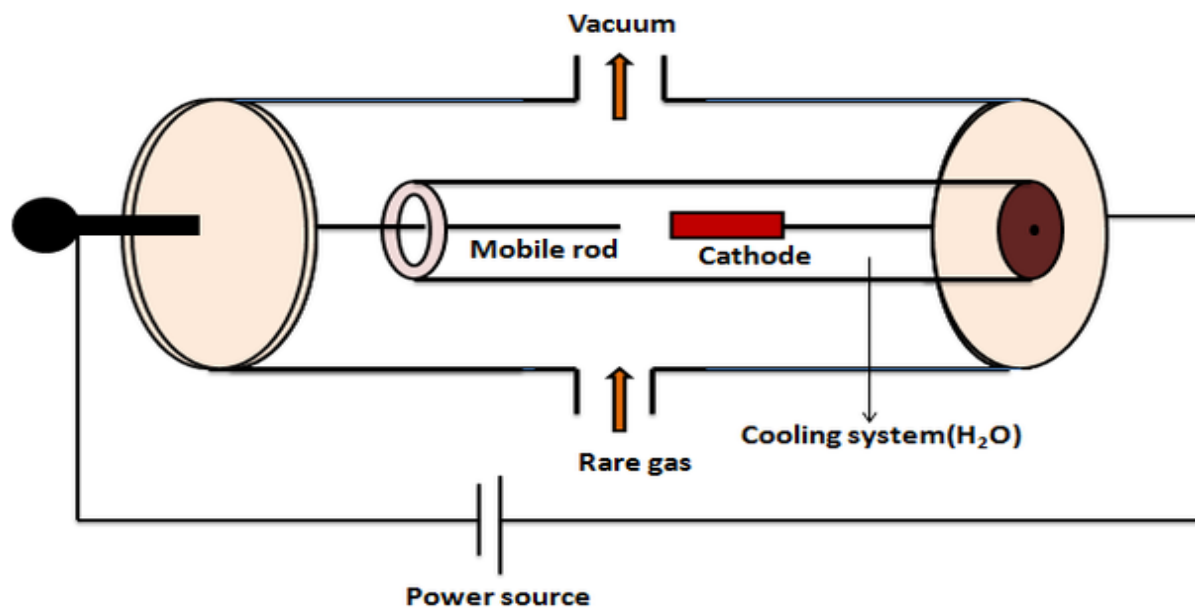
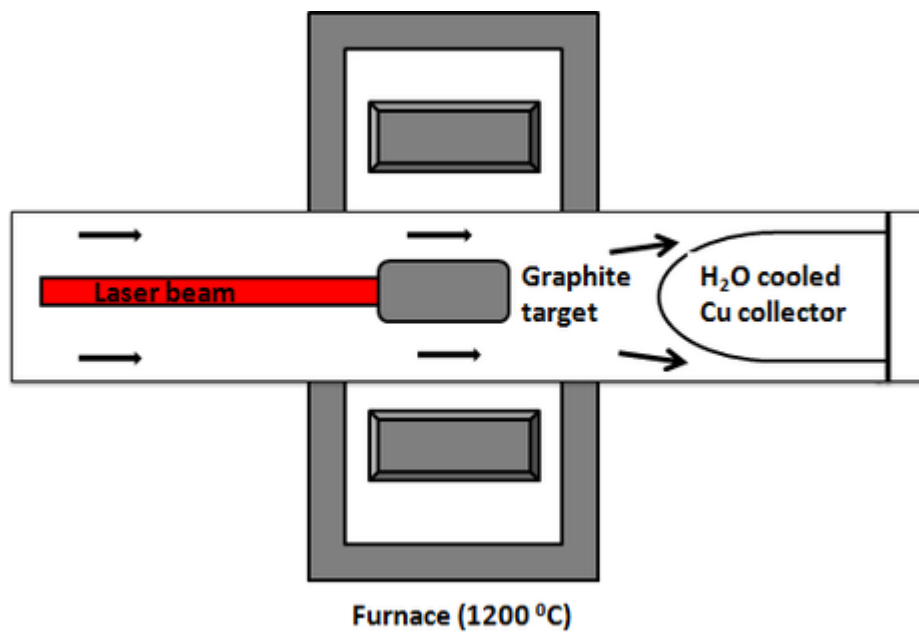


Figure 5. Schematic representation of laser ablation technique for carbon synthesis



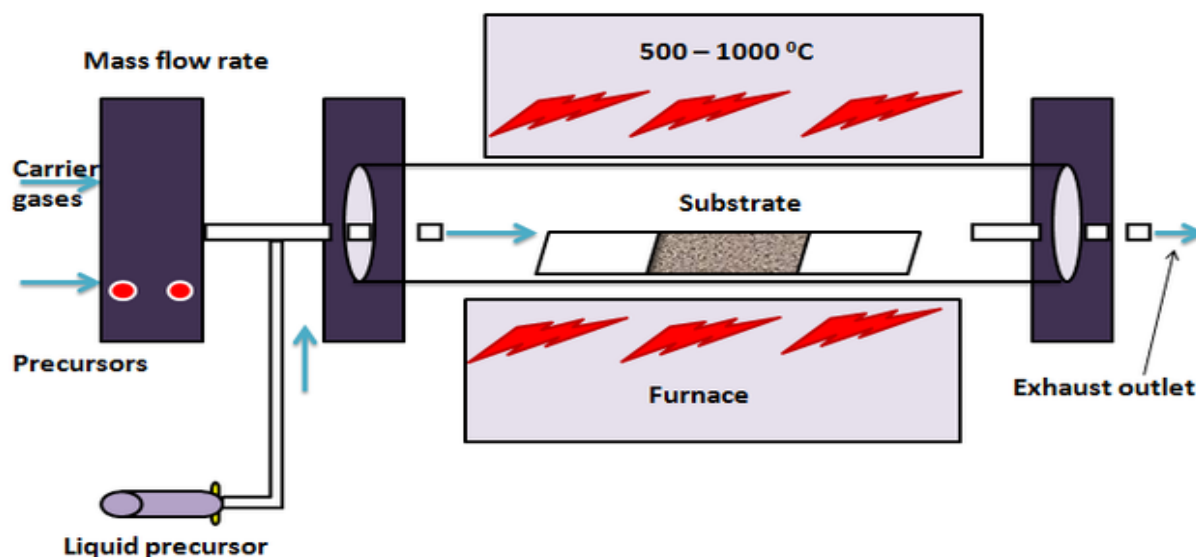
of carbon that is not cost effective as this leads to high-energy consumption and the adhering impurities, which will require further purification of the carbon nanomaterials produced by such methods (Popov et al., 2004).

In view of the above challenges of the two techniques mentioned previously, chemical vapor deposition (Figure 6) is the most commonly used technique. CVD ensure a better control of carbon (e.g. CNT) growth than laser ablation and arc discharge, this makes it a more feasible method (Dai, 2002). It makes use of hydrocarbons as precursors in the presence of metal catalysts at temperature ranging from 500 to 1000 °C. The hydrocarbons get decomposed at this relatively low temperature and thus the growth of CNTs as the system cools. This techniques is simpler in that lower temperature is involved because the precursor is not solid thus consumes less energy (Journet, 1998). Of a vital advantage of CVD worthy of mentioning is that, it is very versatile. Virtually all the major components involved in the growth can be switched; catalyst and precursor can be in liquid or solid form, the particular precursor to be used, possibility of incorporating other materials like nitrogen, temperature and pressure of the reaction etc. (Nikolav et al., 1999). The choice of catalyst plays important role in decomposition and dispersion of liquid hydrocarbon as precursor to allow in situ decomposition. It allows for better dispersion if liquid hydrocarbon is used or in solid form for large-scale synthesis if loaded on large surface area template as well as a well-patterned growth with nanoparticles (Allen et al., 2009; Hart and Slocum, 2006).

Graphene is commonly prepared by four techniques (Anton et al., 2007; EMTSEV, 2009; Reina, 2009; Lomeda, 2008) listed below:

- Direct sonication of graphite or scotch tape approach (known as mechanical cleavage of graphite);
- Growth on SiC (epitaxial);
- Metal substrates CVD;
- Graphite oxide reduction.

Figure 6. Schematic illustration of carbon vapor deposition (CVD)



Some other approaches being reported are; electrochemical process using graphite electrode and unwrapping of carbon nanotubes (Kosynkin et al., 2009; Liu et al., 2008). The most common approach for large-scale preparation is the reduction of graphite oxide by, firstly, oxidize graphite with acids then convert the oxide formed to graphene by reduction. The reduction process can be carried out thermally, chemically or photo catalytically (McAllister et al., 2007; Lomeda et al., 2008; Williams et al., 2008).

## **4. EVALUATION**

### **4.1 Properties**

Carbon nanomaterial, graphene for example, is a monoatomic layer of carbon atoms that is  $sp^2$  hybridized (Geim and Novoselov, 2007). The good electrical properties in ballistic transport of electrons can be traced to its 2D pattern (Novoselov et al., 2004). Graphene also possesses large surface-volume ratio, fast electron transfer mechanism, good tensile strength and very interesting elastic character (Park and Ruoff, 2009; Rao et al., 2009; Yang et al., 2010). A very good stacking is possible with graphene, thus, layers can be varied from single to many of up to 10 layers and the resulting materials are equally interesting.

Multi-walled carbon nanotubes (MWNTs) comprise of several single-walled nanotubes Single-walled carbon nanotubes (SWNTs). The one dimensional SWNTs like graphene sheet (0.4 to 2.0 nm diameter) are rolled-up to form MWNTs (2 to 100 nm diameter) (Baughman et al., 2002; Yang et al., 2010). Largely, MWNTs can possess several surface morphologies such as hollow tubes, stacked cups, carbon filaments etc (Kiselev et al., 1998; Iijima, 1991; Delgado et al., 2008; Allen et al., 2008). The classification of SWNTs can be done based on chiral vectors ( $c_h = na_1 + ma_2 = (n, m)$ ) where  $n$  and  $m$  are integers that correspond to the two graphene vectors (Figure 7) (Avouris, 2002) as shown in Figure 6. The following are few classes:

- Zigzag ( $m = 0$ );
- Arm-chair ( $n = m$ );
- Chiral ( $n \neq m$ ).

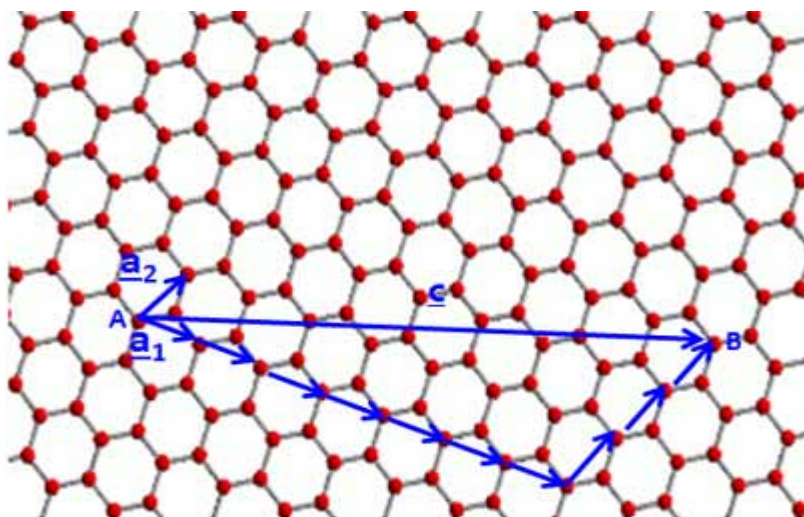
The particular class and vectors provide information about electronic properties; if  $(n - m)$  gives a multiple of 3, then the SWNTs of arm-chair type is metallic.

Depending on the diameter of SWNTs, which have inverse proportionality with band gap, SWNTs are good semiconductors and have metallic character. Normally, MWNTs also have similar characteristics with SWNTS because the effect of a cylinder on its adjacent cylinder is very minute (Baughman et al., 2002; Charlier, 2002). However, the lack of definite control of chiralities for individual nano-cylinders results into MWNTs with SWNTs of different chiralities, thus a metallic properties similar to graphite (turbostratic) will be observed (Cao, 2004).

### **4.2 Applications towards Desulfurization**

The very unique dimensions of CNTs (1-D) and graphene (2-D) are enabling features for their outstanding electrical conductivity and stability. They are of good surface chemistry for easy decoration with desired functionalities, which in turn guaranteed their use in adsorption (desulfurization), electrochemical and

Figure 7. Schematic representation of a graphene sheet with unit hexagonal lattice vectors ( $a_1$  and  $a_2$ )



other applications. This include energy generation via fuel cells and photovoltaic (Brandon et al., 2003; Kauffman et al., 2010), energy storage (batteries, super-capacitors, hydrogen storage) (An et al., 2001) field-effect transistors (Katz, 2004; Kruger et al., 2010) sensors and biosensors (Kauffman and Star, 2008; Ronkainen et al., 2010; Yang et al., 2010). However, there are challenges, like the non-uniformity of materials and their hybrids (Jacobs et al., 2010), lack detailed understanding of structure as related to property and possible contaminants from synthetic precursors/catalysts (Dai, 2002; Kruusma, 2007; Pumera and Miyahara, 2009). These are tasking challenges **but provide an avenue for further detailed studies**. In the following sections, the systems and processes used for desulfurization by carbon-based materials are highlighted.

Graphene and carbon nanotubes are considered good candidates for the removal of liquid phase aromatic sulfur compounds and of gas phase hydrogen sulfide through the adsorption method by metal oxide/graphene or nanotube composites. More specifically, the effects of their oxides as substrates are promising for liquid phase sulfur removal. Their structures that possesses  $\pi$  orbitals can adsorb aromatic sulfur compounds through  $\pi$ - $\pi$  interactions.

#### 4.2.1 Testing Systems

- Batch System:** Adsorptive desulfurization studies of organosulfur compound removal from naphtha (550 ppmS) feed stocks can be carried out in a batch system. The use of adsorbents such as zeolites (5A and 13X) and activated carbon is effective. These two adsorbents (carbon and zeolites) demonstrated a unique performance in their adsorption capabilities; activated carbon has larger capacity but the percentage of sulfur removal (65% at 80 °C) is lower compare to the zeolitic adsorbent with relatively smaller capacity but a larger percentage of sulfur (100% at room temperature and 800g adsorbent/L feed) can be removed. In line with these observations and for industrial application, a two-bed approach gives a better desulfurization process (Salem and Hamid, 1997).

- **Fixed Bed System:** Adsorption studies in a fixed bed set-up can be achieved also with the use of different adsorbents. Alumina, carbon-supported nickel as well as activated carbon can to a large extent remove sulfur and nitrogen from diesel feed with aromatics, nitrogen and sulfur compounds. Activated carbon shows better selectivity in removing refractory sulfur and nitrogen compounds especially with alkylated dibenzothiophene (4, 6-DMDBT) (Kim et al., 2006; Ko et al., 2007). A superior selectivity for nitrogen removal is observed with alumina as compare to the other two adsorbents. This selectivity with alumina is great when basic nitrogen compound is involved hydrocarbon streams.

#### 4.2.2 Types of Desulfurization Process

There is no generalized classification for desulfurization techniques. However, some classification can be made based on the involvement of hydrogen, what happened to sulfur compound during desulfurization and whether desulfurization occurs physically or chemically or both. Considering the change that happened to sulfur compounds; three situations are possible; either the sulfur compounds get decomposed and removed, removed from process stream without decomposing or decomposed only. From the perspective of the hydrogen involvement; a broad classification desulfurization process can be made; hydrodesulfurization (HDS)-based and non HDS-based groups (Babich and Moulijn, 2003). Hydrogen is involved in the decomposition of sulfur compounds for all HDS-based processes while the non HDS-based processes do not involve hydrogen for desulfurization to occur. However, to eliminate sulfur, in most cases, hydrogen is involved with few exceptions as in the case of selective oxidation. Catalytic conversion of sulfur compounds and subsequent removal of sulfur is a well-established desulfurization process. Such processes are hydroprocessing, distillation, extraction, adsorption, oxidation, precipitation, etc. (Figure 8). Their different combinations have been identified as promising.

During the process of desulfurization, sulfur compounds, for instance, benzothiophene or dibenzothiophene can be removed from the stream and then decomposed separately in a vessel. A very low level of sulfur in transportation fuels can be achieved through this process. This process provides an insight for removing sulfur compounds in fuels through distillation with the help of catalysts. It's also possible that some sulfur products (solid or gas) are generated with just decomposition of organosulfur compounds with only the hydrocarbons (without sulfur) remaining in the process stream (example is hydro desulfurization). The last class is just a simple removal of organosulfur compounds from process stream. This can be done by conversion of the organosulfur compounds to different compounds that can be removed easily if direct removal is difficult or impossible; however, disposal of the removed sulfur compounds becomes a great challenge for this type of class. This classification is depicted in Figure 9.

- **Extractive Desulfurization:** Extractive desulfurization employs the use of solubility as the key factor for organosulfur removal. Organosulfur compounds tend to be more soluble in some specific solvents. The sulfur compounds, due to this reason, are transferred from oil feed into the solvent and therefore hydrocarbons are easily separated with the aid of a separator. The sulfur compound free hydrocarbons can now be further charged for the next process or discharged as final product. The mixture of organo-sulfur compounds and the solvent used for it extraction will then be subjected to distillation thus solvent is recovered and can be re-used.

Figure 8. Classification of desulfurization processes base on the nature of the process

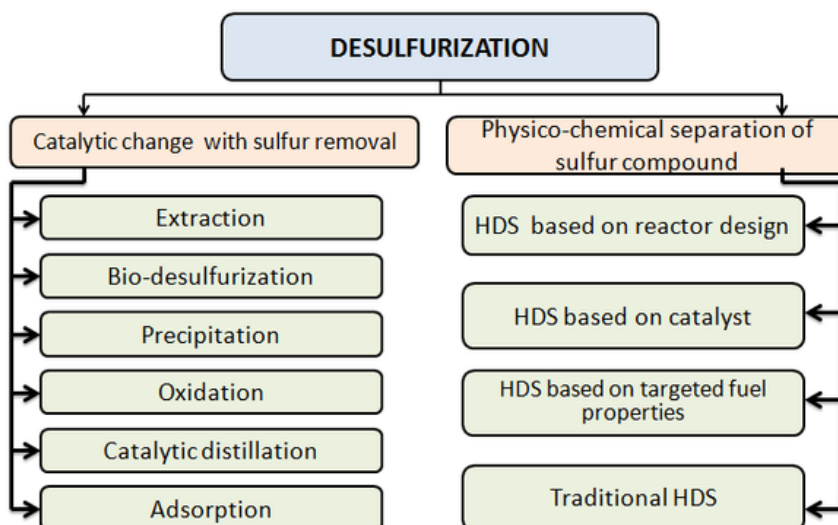
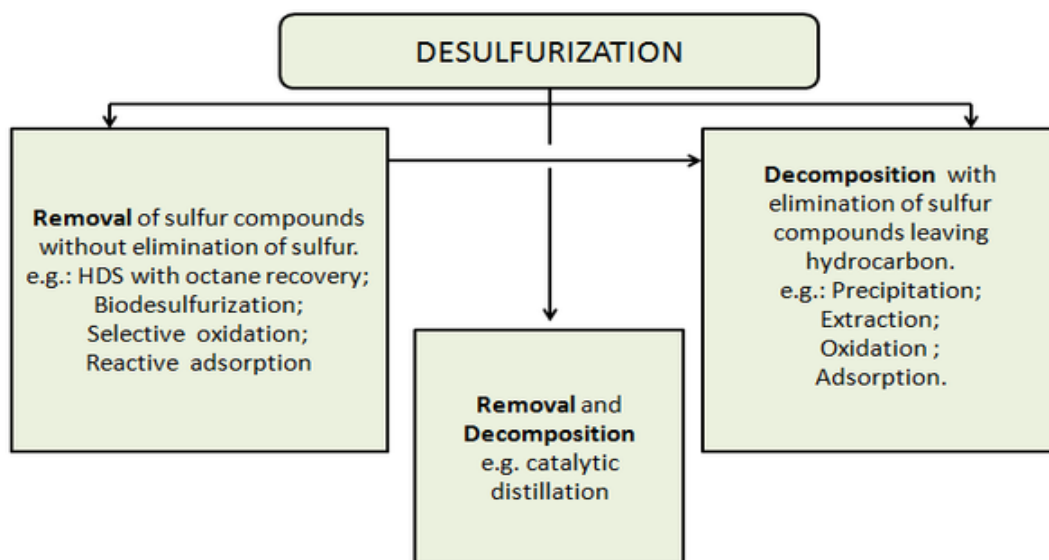


Figure 9. Classification of desulfurization process according to the changes that occur with sulfur compounds



Depending on the number of extraction cycles, several solvents have been identified to be suitable for this purpose with sulfur compound removal of up to 90%. Acetone, glycols, nitrogenous-solvent (Horri, 1996), ethanol are good solvents for extractive desulfurization because they have their boiling points different from those of organo-sulfur compounds and relatively cheap (Forte, 1996; Funakoshi and Aida, 1998).

- **Desulfurization by Precipitation:** Desulfurization can also be achieved via precipitation by forming an insoluble complex of organosulfur compounds and then eliminating them. When a pi acceptor (e.g. tetranitro fluorine) is mixed with alkylated-DBT (e.g. 4, 6-DMDBT) in fuels, an insoluble complex is formed which can be conveniently removed by filtration and the tetranitro fluorine is recovered by adsorption process with the aid of suitable adsorbent (Meille et al., 1997; Milenkovic et al., 1999). This approach does not remove a significant amount of sulfur (< 25%) as some other hydrocarbons in the feed compete in complex formation (Hernandez-Maldonado and Yang, 2004a; 2004b; 2004c).
- **Bio-Desulfurization (BDS):** This process involves the use of micro-organisms (e.g. bacteria) for removal of organosulfur compound. In this process, the sulfur is removed from its parent compound under mild condition and with availability of oxygen and water without degradation of carbon structure present. One very vital feature of this process is that it does not require hydrogen thus a cheaper process than HDS.
- **Selective Oxidative Desulfurization:** Desulfurization by selective oxidation involves oxidation of organosulfur compounds and then purification (Aida et al., 2000). Processes like sulphCo and photochemical desulfurization employ oxidation as a vital operation. Organosulfur compound can be oxidized selectively and processes like adsorption, distillation or decomposition by heating can subsequently be used to separate the oxidized organosulfur compounds from the process stream.

The combination of distillation with selective oxidation is not reported in any literature until date. Considering the principle involved, the approach is promising since sulfones, sulfoxides are the products of oxidation of organosulfur compounds, and they increase their boiling points. (Ford et al., 1997). This process can therefore be likened to the conventional distillation process provided that only separation of organosulfur compounds is desired and subsequent treatment will be done separately. However, the formation of carbonmonoxide and carbon (IV) oxide as by-products and process safety are major issues.

- **Adsorptive Desulfurization:** This is the use of adsorbents for removing sulfur compounds in the fuels. The efficiency of this process lies in the ability of the adsorbents to selectively remove the target sulfur compounds from oil processing stream, durability and regenerability of adsorbent and capacity for adsorption. Desulfurization via adsorption (ADS) can be broadly classified into two based on the nature of interaction of the sulfur compounds and the adsorbent: physical and chemical adsorption. These two classes are briefly explained below.
- **Physical Adsorption (Physisorption):** In physical adsorptive desulfurization, organosulfur compounds adhere to the surface of the solid adsorbent without chemical reaction thus the hydrocarbon refining stream is free of sulfur. Adsorbent regeneration is done by passing suitable solvent on the adsorbent or heating to get rid of adhered sulfur compounds. Several good materials have been used as adsorbents, namely; activated carbon, transition metals supported on zeolites and different metal oxides supported on carbon structures (Ma et al., 2002 and 2005; Velu et al., 2003; Kim et al., 2006). Both denitrogenation and desulfurization can be done simultaneously using activated carbon for adsorption process. For every 1 gram of adsorbent, 0.04 g and 0.1 g of nitrogen and sulfur can be removed from fuel respectively at a temperature close to the room (Sano et al., 2004a; 2004b). Nitrogen and organosulfur compounds are removed in the first stage of the two-step pro-



cess shown in Figure 8. Only very little amount of sulfur is removed at this stage but nitrogen is removed to a large extent. The HDS step removes most of the sulfur and the final adsorption step get rid of remnant nitrogen and sulfur present.

Adsorptive desulfurization processes only decrease the concentration of organosulfur compounds in. Further downstream operation, like hydro processing, needs to be performed at high pressure in order to remove sulfur to achieve ultra-low diesel fuel. For commercial application, certain process parameters have to be set at optimum points. These parameters include but not limited to; fuel feed to adsorbent ratio, particle size of the adsorbent, adsorption cycles, temperature of reactivation etc. To further enhance desulfurization process, a combined adsorption and HDS (Landau et al., 2008) for denitrogenation and desulfurization can be performed as illustrated in Figure 10.

- **Chemical Adsorption (Chemisorptions):** In chemical (reactive) adsorption desulfurization process, the sulfur in the fuel feed combines and reacts to form compound such as hydrogen sulfide ( $H_2S$ ) which is then adsorbed on the surface of the adsorbent (Figure 9). For diesel fuel desulfurization, the reaction to form  $H_2S$  can occur at temperature of 500-700K and pressure of 19-35 bars in the presence of transition metal catalyst. In view of this, many hybrid materials of transition metals supported on carbon, zeolites and several other solid porous materials have been prepared (Slater et al., 2002; Park et al., 2008; Landau et al., 2008). A simple adsorption scheme together with reactivation of spent adsorbent is as illustrated in Figure 11.

## SUMMARY AND OUTLOOK

Recently, there has been a remarkable growth in research on achieving ultra-low sulfur level in transportation fuels. Several research groups from different academic institutions and industrial research

Figure 10. An illustration of combined adsorption and hydrodesulfurization (two-step) process

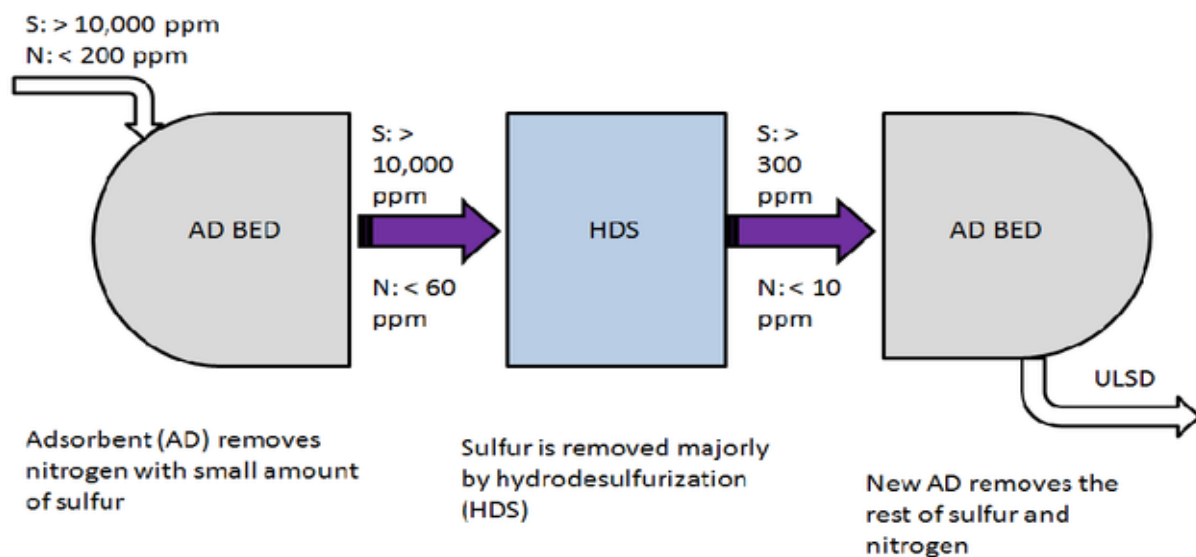
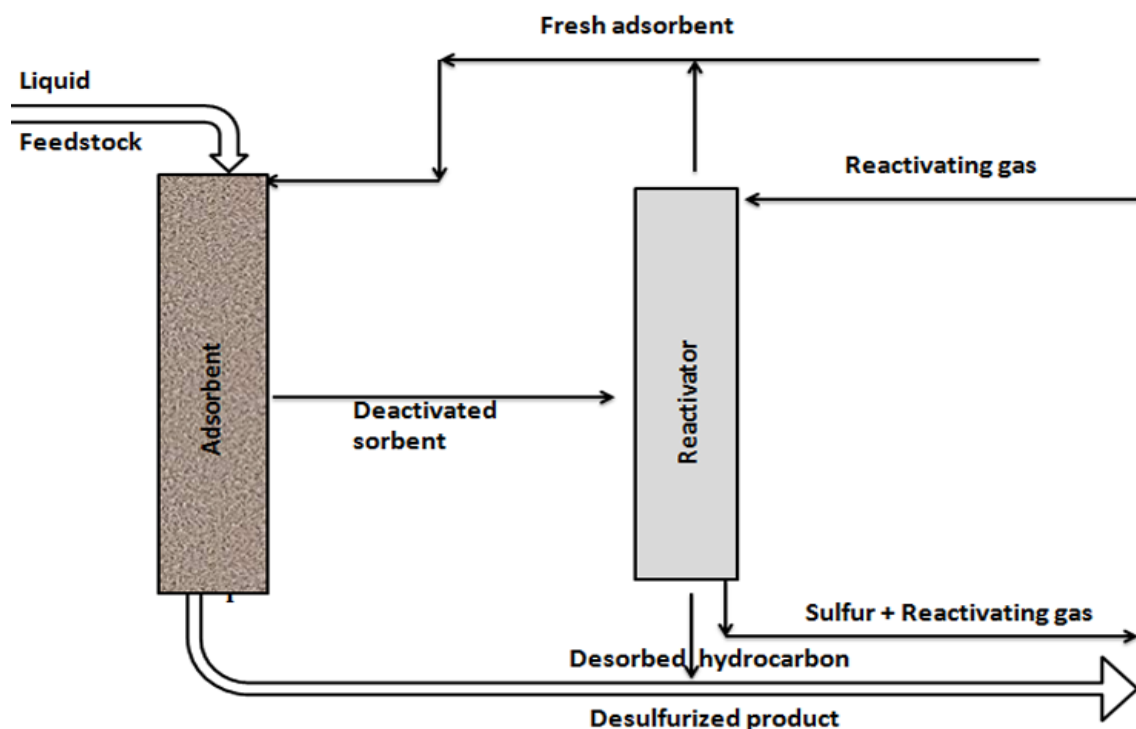


Figure 11. Simplified adsorptive desulfurization process flow



laboratories have published a great number of rich scientific papers. Lower harmful exhaust emissions can easily be achieved with ULSD thereby enhancing air quality. The desulfurization of least active dibenzothiophene (DBT) derivative like 4, 6-DMDBT (sterically hindered) can now be easily achieved by optimizing certain factors such as; kinetics and thermodynamics, feed quality, inhibitory effects, catalytic sites, etc. In the future, the need to produce more volume ULSD from low grade feed stocks like heavy oil and LCO to meet up with the global ULSD demand is pertinent. Other needs like better calorific value, reduced aromatics content and density are also worthy of expectation. These, are challenging, but with enormous economic gain. In order to achieve this great milestone, adsorptive method of desulfurization can play a very big role. ADS does not require hydrogen so it is cheap. It is capable of desulfurizing organ-sulfur compound (e.g. DBT) preferentially. The ADS can be used to achieve a sulfur level of less than 10ppm from the initial sulfur content of 500ppm in diesel fuel.

## ACKNOWLEDGMENT

The authors would like to acknowledge the support provided by King Abdulaziz City for Science and Technology (KACST) through the Science & Technology Unit at King Fahd University of Petroleum & Minerals (KFUPM) for funding this work through project No. 13-PET393-04 as part of the National Science, Technology and Innovation Plan.

## REFERENCES

- Agarwal, P., & Sharma, D. K. (2010). Comparative studies on the biodesulfurization of crude oil with other desulfurization techniques and deep desulfurization through integrated processes. *Energy & Fuels*, 24(1), 518–524. doi:10.1021/ef900876j
- Aida, T., Yamamoto, D., Iwata, M., & Sakata, K. (2000). Development of oxidative desulfurization process for diesel. *Review on Heteroatom Chemistry*, 22, 241–256.
- Allen, B. L., Kichambare, P. D., & Star, A. (2008). Synthesis, characterization, and manipulation of nitrogen-doped carbon nanotube cups. *ACS Nano*, 2(9), 1914–1920. doi:10.1021/nn800355v PMID:19206432
- Allen, B. L., Shade, C. M., Yingling, A. M., Petoud, S., & Star, A. (2009). Graphitic nanocapsules. *Advanced Materials*, 21, 4692–4695.
- An, K. H., Kim, W. S., Park, Y. S., Moon, J.-M., Bae, D. J., & Lim, S. C. et al. (2001). Electrochemical Properties of High-Power Supercapacitors Using Single-Walled Carbon Nanotube Electrodes. *Journal of Advanced Functional Materials (Basel)*, 11, 387–392.
- Anbia, M., & Parvin, Z. (2011). Desulfurization of fuels by means of a nanoporous carbon adsorbent. *Chemical Engineering Research & Design*, 89(66A), 641–647. doi:10.1016/j.cherd.2010.09.014
- Anton, N. S., Mehdi, M. Y., Romaneh, J., Ouseph, P. J., Cohn, R. W., & Sumanasekera, G. U. (2007). Electrostatic deposition of graphene. *Nanotechnology*, 18, 13530–13534. PMID:21730375
- Atanasova, P., Vladov, Ch., Halachev, T., Fierro, J. L. G., & López, A. A. (1995). Influence on the phosphorus concentration and the method of preparation on the hydrodesulfurization activity of P-Ni-W/alumina catalysts. *Bulletin des Sociétés Chimiques Belges*, 104(4), 219–223.
- Avouris, P. (2002). Molecular electronics with carbon nanotubes. *Accounts of Chemical Research*, 35(12), 1026–1034. doi:10.1021/ar010152e PMID:12484790
- Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, 82(6), 607–631. doi:10.1016/S0016-2361(02)00324-1
- Babich, I. V., & Moulijn, J. V. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, 82(6), 607–631. doi:10.1016/S0016-2361(02)00324-1
- Bai, S., & Shen, X. (2012). Graphene-inorganic nanocomposites. *Royal Society of Chemistry Advances*, 2, 64–98.
- Baker, R. T. K. (1995). A review of in-situ electron microscopy studies of metal/metal oxide graphite interactions. *Journal of Adhesion and Adhesives*, 52(1-4), 13–40.
- Baker, R. T. K., & Chludzinski, J. J. Jr. (1981). Catalytic gasification of graphite by chromium and copper in oxygen, steam and hydrogen. *Carbon*, 19(2), 75–82. doi:10.1016/0008-6223(81)90110-X
- Baughman, R. H., Zakhidov, A. A., & de Heer, W. A. (2002). Carbon nanotubes--the route towards applications. *Science*, 297(5582), 787–792. doi:10.1126/science.1060928 PMID:12161643

- Bernier, P., & Ajayan, P. M. (1994). Application of Carbon Nanotubes as Supports in Heterogeneous Catalysis. *Journal of the American Chemical Society*, 116(17), 7935–7936. doi:10.1021/ja00096a076
- Bhatia, S., & Sharma, D. K. (2006). Emerging role of bio-refining of heavier crude oils and integration of bio-refining with petroleum refineries in the future. *Petroleum Science and Technology*, 24(10), 1125–1159. doi:10.1080/10916460600817447
- Blanco-López, M. C., Gutiérrez-Fernández, C., Lobo-Castañón, M. J., Miranda-Ordieres, A. J., Tuñón-Blanco, P. (2004). Electrochemical sensing with electrodes modified with molecularly imprinted polymer films. *Analytical and Bioanalytical Chemistry*, 378(8), 1922–1928.
- Brandon, N. P., Skinner, S., & Steele, B. C. (2003). Recent advances in materials for fuel cells. *Annual Review of Materials Research*, 33(1), 183–213. doi:10.1146/annurev.matsci.33.022802.094122
- Cao, G. (2004). *Nanostructures and Nanomaterials: Synthesis, properties and applications*. United Kingdom: Imperial College. doi:10.1142/p305
- Charlier, J. C. (2002). Defects in carbon nano tubes. *Accounts of Chemical Research*, 35(12), 1063–1069. doi:10.1021/ar010166k PMID:12484794
- Cheng, G., & Guo, T. (2002). Surface segregation in Ni/Co bimetallic nanoparticles produced in single-walled carbon nanotube synthesis. *The Journal of Physical Chemistry B*, 106(23), 5833–5839. doi:10.1021/jp025530r
- Cui, R. L., Zhang, Y., Wang, J. Y., Zhou, W. W., & Li, Y. (2010). Comparison between copper and iron as catalyst for chemical vapor deposition of horizontally aligned ultralong single-walled carbon nanotubes on silicon substrates. *Journal of Physical Chemistry*, 114(37), 15547–15552.
- Daenen, M., De Fouw, R., Hamers, B., Janssen, P., Schouteden, K., & Veld, M. (2003). The Wondrous World of Carbon Nanotubes. A Review of Current Carbon Nanotube Technologies. Eindhoven University of Technology, 89.
- Dai, H. (2002). Carbon nanotubes: Opportunities and challenges. *Surface Science*, 500(1-3), 218–241. doi:10.1016/S0039-6028(01)01558-8
- Daimler–Chrysler AG. (2000). Method for desulfurization engine fuel on board a motor vehicle // W.O 2000/20531.
- De Volder, M. F. L., Tawfick, S. H., Baughman, R. H., & Hart, A. J. (2013). Carbon nanotubes: Present and future commercial applications. *Science*, 339(6119), 535–539. doi:10.1126/science.1222453 PMID:23372006
- Deck, C. P., & Vecchio, K. (2006). Prediction of carbon nanotube growth success by the analysis of carbon-catalyst binary phase diagrams. *Carbon*, 44(2), 267–275. doi:10.1016/j.carbon.2005.07.023
- Delgado, J. L., Herranz, M. A., & Martin, N. (2008). The nano-forms of carbon. *Journal of Materials Chemistry*, 18(13), 1417–1426. doi:10.1039/b717218d

- Delitala, C., Cadoni, E., Delpiano, D., Meloni, D., Melis, S., & Ferino, I. (2008). Liquid-phase thiophene adsorption on MCM-22 zeolite and activated carbon. *Microporous and Mesoporous Materials*, 110(2-3), 197–215. doi:10.1016/j.micromeso.2007.06.018
- Ding, F., Larsson, P., Larsson, J. A., Ahuja, R., Duan, H. M., Rosen, A., & Bolton, K. (2008). The importance of strong carbon-metal adhesion for catalytic nucleation of single-walled carbon nanotubes. *Nano Letters*, 8(2), 63–68. doi:10.1021/nl072431m PMID:18162001
- Ding, M., Tang, Y., & Star, A. (2012). Understanding Interfaces in Metal–Graphitic Hybrid Nanostructures. *The Journal of Physical Chemistry Letters*, 4(1), 147–160. doi:10.1021/jz301711a
- Dribinskii, A. V., Tarasevich, M. R., & Kazarinov, V. E. (1989). Electrocatalysis on carbon materials. *Materials Chemistry and Physics*, 22(3-4), 377–400. doi:10.1016/0254-0584(89)90006-0
- Ebbesen, T. W., & Ajayan, P. M. (1992). Large scale synthesis of carbon nanotubes. *Nature*, 358(6383), 220–222. doi:10.1038/358220a0
- Ebbesen, T. W., Hiura, H., Bisher, M. E., Treacy, M. M. J., Shreeve-Keyer, J. L., & Haushalter, R. C. (1996). Decoration of carbon nano tubes. *Advanced Materials*, 8(2), 155–157. doi:10.1002/adma.19960080212
- Edwards, R. S., & Coleman, K. S. (2013). Graphene film growth on polycrystalline metals. *Accounts of Chemical Research*, 46(1), 23–30. doi:10.1021/ar3001266 PMID:22891883
- Emtsev, K. V., Bostwick, A., Horn, K., Jobst, J., Kellogg, G. L., & Ley, L. et al. (2009). Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nature Materials*, 8(3), 203–207. doi:10.1038/nmat2382 PMID:19202545
- Ford, J. F., Rayne, T. A., & Adlington, D. G. (1967). Desulfurization of hydrocarbons using oxidative and hydro-treatments. *US Patent*, 3341448.
- Forte, P. (1996). Process for the Removal of Sulfur from Petroleum Fractions. *US Patent*, 5582714.
- Funakoshi, I., & Aida, T. (1998). Process for recovering organic sulfur compounds from fuel oil. *US Patent*, 5753102.
- Gates, B. C., & Tropsoe, H. (1997). Reactivity in deep catalytic hydro-desulfurization: Challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Polyhedron*, 16(18), 3213–3217. doi:10.1016/S0277-5387(97)00074-0
- Geim, A. K. (2009). Graphene: Status and prospects. *Science*, 324(5934), 1530–1534. doi:10.1126/science.1158877 PMID:19541989
- Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene. *Nature Materials*, 6(3), 183–191. doi:10.1038/nmat1849 PMID:17330084
- Hart, A. J., & Slocum, A. H. (2006). Rapid growth and flow-mediated nucleation of millimeter-scale aligned carbon nanotube structures from a thin-film catalyst. *The Journal of Physical Chemistry B*, 110(16), 8250–8257. doi:10.1021/jp055498b PMID:16623503

- Hernandez, Y., Nicolosi, V., Lotya, M., Blighe, F. M., Sun, Z., & De, S. et al. (2008). High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotechnology*, 3(9), 563–568. doi:10.1038/nnano.2008.215 PMID:18772919
- Hernandez-Maldonado, A. J., Stamatis, S. D., Yang, R. T., He, A. Z., & Cannella, W. (2004). New sorbents for desulfurization of diesel fuels via pi-complexation: Layered beds and regeneration. *Industrial & Engineering Chemistry Research*, 43(3), 769–776. doi:10.1021/ie034108+
- Hernandez-Maldonado, A. J., & Yang, R. T. (2003). Desulfurization of commercial liquid fuels by selective adsorption via pi-complexation with Cu(I)-Y zeolite. *Industrial & Engineering Chemistry Research*, 42(31), 4231–4239.
- Hernandez-Maldonado, A. J., & Yang, R. T. (2004a). Desulfurization of diesel fuels by adsorption via pi-complexation with vapor phase exchanged (VPIE) Cu(I)-Y zeolites. *Journal of the American Chemical Society*, 126(4), 992–993. doi:10.1021/ja039304m PMID:14746446
- Hernandez-Maldonado, A. J., & Yang, R. T. (2004b). Desulfurization of diesel fuels via pi-complexation with nickel(II)-exchanged X- and Y-zeolites. *Industrial & Engineering Chemistry Research*, 43(4), 1081–1089. doi:10.1021/ie034206v
- Hernandez-Maldonado, A. J., & Yang, R. T. (2004c). New sorbents for desulfurization of diesel fuels via pi-complexation. *The American Institute of Chemical Engineers Journal*, 50, 791–801. doi:10.1002/aic.10074
- Horii, Y., Onuki, H., Doi, S., Mori, T., Takatori, T., Sato, H., et al. (1996). Desulfurization and denitration of light oil by extraction. *US Patent*, 5494572.
- Hsu, W. K.; Terrones, M.; Hare, J. P.; Terrones, H.; Kroto, H. W.; Walton, D. R. M. Electrochemical formation of carbon nanostructures. *Chemical Physics Letters*, 262, 161-166.
- Huang, X., Qi, X., Boey, F., & Zhang, H. (2012). Graphene-based composites. *Chemical Society Reviews*, 41(2), 666–686. doi:10.1039/C1CS15078B PMID:21796314
- Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, 354(6348), 56–58. doi:10.1038/354056a0
- Irvine, R. L. (1998). Process for desulfurizing gasoline and hydrocarbon feedstocks. *US Patent*, 5730860.
- Irvine, R. L., Benson, B. A., Varraveto, D. M., & Frye, R. A. NPRA (1999, March 21-23). Proceedings of the *Annual Meeting*, AM-99-42, San Antonio, Texas.
- Irvine, R. L., Varraveto, D. M. (1999). Adsorption process for nitrogen and sulfur. *Petroleum Technology Quarterly Summer* 3, 37- 40.
- Ivanov, V., Fonseca, A., Nagy, J. B., Lucas, A., Lambin, P., Bernaerts, D., & Zhang, X. B. (1995). Catalytic production and purification of nanotubules having fullerene-scale diameters. *Carbon*, 33(12), 1727–1738. doi:10.1016/0008-6223(95)00132-1
- Iwamoto, R., & Grimblot, J. (1997). Acidity and hydrogenation properties of Mo-P-alumina catalysts prepared by a sol-gel method. *Journal of Catalysis*, 172(1), 252–255. doi:10.1006/jcat.1997.1855

- Jacobs, C. B., Peairs, M. J., & Venton, B. J. (2010). Carbon nanotubes electrochemical sensors for bio-molecules. *Analytica Chimica Acta*, 662(2), 105–127. doi:10.1016/j.aca.2010.01.009 PMID:20171310
- Jourdain, V., & Bichara, C. (2013). Current understanding of the growth of carbon nanotubes in catalytic chemical vapour deposition. *Carbon*, 58, 2–39. doi:10.1016/j.carbon.2013.02.046
- Journet, C., Bernier, P. (n. d.). Production of carbon nanotubes. *Journal of Applied Physics A*, 67, 1-9.
- Journet, C., Maser, W. K., Bernier, P., Loiseau, A., de la Chapelle, M. L., & Lefrant, S. et al. (1997). Large-scale production of single-walled carbon nanotubes by the electric-arc technique. *Nature*, 388(6644), 756–758. doi:10.1038/41972
- Katz, H. E. (2004). Chemically Sensitive Field-Effect Transistors and Chemiresistors: New Materials and Device. Structures. *Journal of Electroanalytical Chemistry*, 16(22), 1837–1842. doi:10.1002/elan.200403071
- Kauffman, D. R., Shade, C. M., Uh, H., Petoud, S., & Star, A. (2009). Decorated carbon nanotubes with unique oxygen sensitivity. *Nature Chemistry*, 1(6), 500–506. doi:10.1038/nchem.323 PMID:21378918
- Kauffman, D. R., & Star, A. (2008). Carbon Nanotube Gas and Vapor Sensors. *Angewandte Chemmie International Edition*, 47(35), 6550-6570.
- Kauffman, D. R., Tang, Y., Kichambare, P. D., Jackovitz, J. F., & Star, A. (2010). Long-Term Performance of Pt-Decorated Carbon Nanotube Cathodes in Phosphoric Acid Fuel Cells. *Energy & Fuels*, 24(3), 1877–1881. doi:10.1021/ef100013v
- Kim, J. H., Ma, X., Zhou, A., & Song, C. (2006). Ultra clean desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: A study on adsorptive selectivity and mechanism. *Catalysis Today*, 111(1-2), 74–83. doi:10.1016/j.cattod.2005.10.017
- Kinoshita, K., & Bett, J. A. S. (1973). Potentiodynamic analysis of surface oxides on carbon blacks. *Carbon*, 11(4), 403–411. doi:10.1016/0008-6223(73)90080-8
- Kiselev, N. A., Sloan, J., Zakharov, D. N., Kukovitskii, E. F., Hutchison, J. L., Hammer, J., & Kotosonov, A. S. (1998). Carbon nanotubes from polyethylene precursors: Structure and structural changes as revealed by HREM. *Carbon*, 36, 1149–1157. doi:10.1016/S0008-6223(98)00092-X
- Kongkanand, A., Martínez Domínguez, R., & Kamat, P. V. (2007). Single wall carbon nanotube scaffolds for photoelectrochemical solar cells. capture and transport of photogenerated electrons. *Nano Letters*, 7(3), 676–680. doi:10.1021/nl0627238 PMID:17309316
- Kosynkin, D. V., Higginbotham, A. L., Sinitskii, A., Lomeda, J. R., Dimiev, A., Price, B. K., & Tour, J. M. (2009). Mechanically Assisted Exfoliation and Functionalization of Thermally Converted Graphene Sheets. *Nature*, 458, 872–876. doi:10.1038/nature07872 PMID:19370030
- Kruger, M., Buitelaar, M. R., Nussbaumer, T., Schonenberger, C., & Forro, L. (2001). Electrochemical carbon nanotube field-effect transistor. *Applied Physics Letters*, 78(9), 1291–1293. doi:10.1063/1.1350427

- Kruusma, J., Mould, N., Jurkschat, K., Crossley, A., & Banks, C. E. (2007). Single walled carbon nanotubes contain residual iron oxide impurities which can dominate their electrochemical activity. *Electrochemistry Communications*, 9(9), 2330–2333. doi:10.1016/j.elecom.2007.06.024
- Kumar, S., Srivastava, V. C., & Badoni, R. P. (2012). Oxidative desulfurization by chromium promoted sulfated zirconia. *Fuel Processing Technology*, 93(1), 18–25. doi:10.1016/j.fuproc.2011.08.017
- Kymakis, E., & Amaratunga, G. (2007). Single-wall carbon nanotube/conjugated polymer photovoltaic devices. *Applied Physics Letters*, 80(1), 112–114. doi:10.1063/1.1428416
- Lam, V., Li, G., Song, C., Chen, J., Fairbridge, C., Hui, R., & Zhang, J. (2012). A review of electrochemical desulfurization technologies for fossil fuels. *Fuel Processing Technology*, 98, 30–38. doi:10.1016/j.fuproc.2012.01.022
- Laplace, D., Bernier, P., Maser, W. K., Flamant, G., Guillard, T., & Loiseau, A. (1998, January). Carbon nanotubes: The solar approach. *Carbon*, 36(5-6), 685–688. doi:10.1016/S0008-6223(98)00025-6
- Lee, C., Wei, X., Kysar, J. W., & Hone, J. (2008). Measurement of the elastic properties and intrinsic Strength of monolayer graphene. *Science*, 321(5887), 385–388. doi:10.1126/science.1157996 PMID:18635798
- Lemaire, M. (1999). *Energy & Fuels*, 13, 881. doi:10.1021/ef980262a
- Li, D.-C., Dai, L., Huang, S., Mau, A. W. H., & Wang, Z. L. (2000). Structure and growth of aligned carbon nanotube films by pyrolysis. *Chemical Physics Letters*, 316(5-6), 349–355. doi:10.1016/S0009-2614(99)01334-2
- Li, J. (2009). In P. Serp & J. L. Figueiredo (Eds.), *Carbon Materials for Catalysis* (pp. 507–533).
- Li, W. Z., Xie, S. S., Qian, L. X., Chang, B. H., Zou, B. S., & Zhou, W. Y. et al. (1996). Large scale synthesis of aligned carbon nanotubes. *Science*, 274(5293), 1701–1703. doi:10.1126/science.274.5293.1701 PMID:8939858
- Li, X., Cai, W., An, J., Kim, S., Nah, J., & Yang, D. et al. (2009). Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science*, 324(5932), 1312–1314. doi:10.1126/science.1171245 PMID:19423775
- Li, X., Qin, Y., Picraux, S. T., & Guo, Z.-X. (2011). Noncovalent assembly of carbon nanotube-inorganic hybrids. *Journal of Materials Chemistry*, 21(21), 7527–7547. doi:10.1039/c1jm10516g
- Li, Y., Cui, R. L., Ding, L., Liu, Y., Zhou, W. W., & Zhang, Y. et al. (2010). How catalysts affect the growth of single-walled carbon nanotubes on substrates. *Advanced Materials*, 22(13), 1508–1515. doi:10.1002/adma.200904366 PMID:20437500
- Liu, N., Luo, F., Wu, H., Liu, Y., Zhang, C., & Chen, J. (2008). One-step ionic-liquid-assisted electrochemical synthesis of ionic-liquid-functionalized graphene sheets directly from graphite. *Advanced Functional Materials*, 18(10), 1518–1525. doi:10.1002/adfm.200700797
- Lomeda, J. R., Doyle, C. D., Kosynkin, D. V., Hwang, W. F., & Tour, J. M. (2008). Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets. *Journal of the American Chemical Society*, 130(48), 16201–16206. doi:10.1021/ja806499w PMID:18998637



- Loo, A. H., Bonanni, A., & Pumera, M. (2013). Biorecognition on graphene: Physical, covalent, and affinity immobilization methods exhibiting dramatic differences. *Asian Journal of Chemistry*, 8(1), 198–203. doi:10.1002/asia.201200756 PMID:23090869
- Ma, X., & Schobert, H. H. (2000). Molecular simulation on hydrodesulfurization of Thiophenic compounds over  $\text{MoS}_2$  using ZINDO. *Journal of Molecular Catalysis A Chemical*, 160(2), 409–427. doi:10.1016/S1381-1169(00)00278-8
- Ma, X., Sun, L., & Song, C. (2002). A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. *Catalysis Today*, 77(1-2), 107–116. doi:10.1016/S0920-5861(02)00237-7
- Ma, X., Velu, S., Kim, J. H., & Song, C. (2005). Deep desulfurization of gasoline by selective adsorption over solid adsorbents and impact of analytical methods on ppm level sulfur quantification for fuel cell applications. *Applied Catalysis B: Environmental*, 56(1-2), 137–147. doi:10.1016/j.apcatb.2004.08.013
- Matsui, M., Horiba, T., Yamamoto, O., Takeda, Y., Seki, N., & Imanishi, N. (2013). Carbon paper substrate for silicon-carbon composite anodes in lithium-ion batteries. *Journal of Power Sources*, 241, 744–750. doi:10.1016/j.jpowsour.2013.05.090
- Mattevi, C., Kim, H., & Chhowalla, M. (2011). A review of chemical vapour deposition of graphene on copper. *Journal of Materials Chemistry*, 21(10), 3324–3334. doi:10.1039/C0JM02126A
- Mc Allister, M. J., Li, J.-L., Adamson, D. H., Schniepp, H. C., Abdala, A. A., & Liu, J. et al. (2007). Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chemistry of Materials*, 19(18), 4396–4404. doi:10.1021/cm0630800
- McEuen, P. L., Fuhrer, M. S., & Park, H. K. (2002). Single-walled carbon nanotube electronics. *IEEE Transactions on Nanotechnology*, 1(1), 78–85. doi:10.1109/TNANO.2002.1005429
- Meille, V., Shulz, E., Vrinat, M., & Lemaire, M. (1997). Hydrodesulfurization of alkyl dibenzothiophenes over a  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalyst: Kinetics and mechanism. *Journal of Catalysis*, 170(1), 29–36. doi:10.1006/jcat.1997.1732
- Milenkovic, A., Shulz, E., Meille, V., Lofferda, D., Forissier, M., Vrinat, M., & Sautet, P. (2004). Charge transfer complexes between tetranitrofluorenone and polyaromatic compounds from gasoil: A combined DFT and experimental study. *Physical Chemistry*, 6, 1169–1180.
- Molina-Ontoria, A., Chaur, M. N., Plonska-Brzezinska, M. E., & Echegoyen, L. (2013a). Preparation and characterization of soluble carbon nano-onions by covalent functionalization, employing a Na-K alloy. *Chemical Communications (Cambridge)*, 49(24), 2406–2408. doi:10.1039/c3cc39077b PMID:23411670
- Nagai, M., Goto, Y., Ishii, H., & Omi, S. (2000). XPS and TPSR study of nitrated molybdena-alumina catalyst for the hydrodesulfurization of dibenzothiophene. *Applied Catalysis A, General*, 192(2), 189–199. doi:10.1016/S0926-860X(99)00341-5
- Naidich, J. V. (1981). The wettability of solids by liquid metals. *Progress in Surface Membrane Science*, 14, 353–484. doi:10.1016/B978-0-12-571814-1.50011-7

- Nikolaev, P., Smalley, R. E., Bronikowski, M. J., Bradley, R. K., Rohmund, F., Colbert, D. T., & Smith, K. A. (1999). Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chemical Physics Letters*, 313(1-2), 91–97. doi:10.1016/S0009-2614(99)01029-5
- Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., & Dubonos, S. V. (2004). Electric field effect in atomically thin carbon films. *Science*, 306(5696), 666–669. doi:10.1126/science.1102896 PMID:15499015
- Park, J. G., Ko, C. H., Yi, K. B., Park, J. H., Han, S. S., Cho, S. H., & Kim, J. N. (2008). Reactive adsorption of sulfur compounds in diesel on nickel supported on mesoporous silica. *Applied Catalysis B: Environmental*, 81(3-4), 244–250. doi:10.1016/j.apcatb.2007.12.014
- Park, S., & Ruoff, R. S. (2009). Chemical methods for the production of graphenes. *Nature Nanotechnology*, 4(4), 217–224. doi:10.1038/nnano.2009.58 PMID:19350030
- Perathoner, S., Gangeri, M., Lanzafame, P., & Centi, G. (2007). Nanostructured electrocatalytic Pt-carbon materials for fuel cells and CO<sub>2</sub> conversion. *Kinetics and Catalysis*, 48(6), 877–883. doi:10.1134/S0023158407060171
- Popov, V. N. (2004). Carbon nanotubes: Properties and applications. *Materials Science and Engineering R Reports*, 43(3), 61–102. doi:10.1016/j.msar.2003.10.001
- (2001). Quality requirements for liquid fuels [in Estonian]. *State Announcer. App.*, 66, 2765–2775.
- Rana, M. S., Sa'mano, V., Ancheyta, J., & Diaz, J. A. I. (2007). A review of recent advances on processing technologies for upgrading of heavy oils and residual. *Fuel*, 86(9), 1216–1231. doi:10.1016/j.fuel.2006.08.004
- Rao, C. N. R., Sood, A. K., Subrahmanyam, K. S., & Govindaraj, A. (2009). Graphene: The new two-dimensional nanomaterial. *Angewandte Chemie International Edition*, 48(42), 7752–7777. doi:10.1002/anie.200901678 PMID:19784976
- Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., & Bulovic, V. et al. (2009). Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Letters*, 9(1), 30–35. doi:10.1021/nl801827v PMID:19046078
- Ronkainen, N. J., Halsall, H. B., & Heineman, W. R. (2010). Electrochemical biosensors. *Chemical Society Reviews*, 39(5), 1747–1763. doi:10.1039/b714449k PMID:20419217
- Salem, A. B. S. H. (1994). Naphtha desulfurization by adsorption. *Industrial & Engineering Chemistry Research*, 33(2), 336–340. doi:10.1021/ie00026a025
- Salem, A. B. S. H., & Hamid, H. S. (1997). Removal of sulfur compounds from naphtha solutions using solid adsorbents. *Chemical Engineering & Technology*, 20(5), 342–347. doi:10.1002/ceat.270200511
- Salernitanoa, E., Giorgi, L., & Dikonimos, M. (2014). Direct growth of carbon nanofibers on carbon-based substrates as integrated gas diffusion and catalysts layer for polymer electrolytes fuel cells. *International Journal of Hydrogen Energy*, 39(27), 15005–15016. doi:10.1016/j.ijhydene.2014.07.060

Sano, Y. (2004a). Adsorptive removal of sulfur and nitrogen species from a straight run gas oil over activated carbons for its deep hydrodesulfurization. *Applied Catalysis B: Environmental*, 49(4), 219–225. doi:10.1016/j.apcatb.2003.12.007

Sano, Y., Choi, K. K., Korai, Y., & Mochida, I. (2004b). Selection further activation of activated carbons for removal of nitrogen species in gas oil as a pretreatment for its deep hydrodesulfurization. *Energy & Fuels*, 18(3), 644–651. doi:10.1021/ef034080e

Sano, Y., Sugahara, K., Choi, K. H., Korai, Y., & Mochida, I. (2005). Two-step adsorption process for deep desulfurization of diesel oil. *Fuel*, 84(7-8), 903–910. doi:10.1016/j.fuel.2004.11.019

Savage, D. W., Kaul, B. K., Dupre, G. D., O'Bara, J. T., Wales, W. E., & Ho, T. C. (1995). Deep desulfurization of distillate fuels. *US Patent*, 5454933.

Schlapbach, L., & Züttel, A. (2001). Hydrogen-storage materials for mobile applications. Hydrogen-storage materials for mobile applications. *Nature*, 414(6861), 353–358. doi:10.1038/35104634 PMID:11713542

Seah, C. M., Chai, S. P., & Mohamed, A. R. (2014). Mechanisms of graphene growth by chemical vapour deposition on transition metals. *Carbon*, 70, 1–21. doi:10.1016/j.carbon.2013.12.073

Seredych, M., Lison, J., Jans, U., & Bandosz, T. J. (2009). Textural and chemical factors affecting adsorption capacity of activated carbon in highly efficient desulfurization of diesel fuel. *Carbon*, 47(10), 2491–2500. doi:10.1016/j.carbon.2009.05.001

Shafi, R., & Hutchings, G. J. (2000). Hydrodesulfurization of hindered dibenzothiophenes:an overview. *Catalysis Today*, 59(3-4), 423–442. doi:10.1016/S0920-5861(00)00308-4

Shin, W. H., Jeong, H. M., Kim, B. G., Kang, J. K., & Choi, J. W. (2012). Nitrogen-doped multi-walled carbon nanotubes for lithium storage with extremely high capacity. *Nano Letters*, 12(5), 2283–2288. doi:10.1021/nl3000908 PMID:22452675

Sinnott, S. B., & Andrews, R. (2001). Carbon nanotubes: Synthesis, properties and applications. *Critical Reviews in Solid State and Material Sciences*, 26(3), 145–249. doi:10.1080/20014091104189

Song, C. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today*, 86(1-4), 211–263. doi:10.1016/S0920-5861(03)00412-7

Stephanie, N. S., Goubert, R., Xiuling, Z., & Andrzej, W. (2010). Synthesis and characterization of carbon-supported transition metal oxide nanoparticles-Cobalt porphyrin as catalysts for electroreduction of oxygen in acids. *Electrochemistry Communications*, 12(11), 1457–1461. doi:10.1016/j.elecom.2010.06.004

Sundaraman, R., Peduzzi, E., & Song, C. (2009). Catalytic cracking of oxidized sulfur compounds in gas oil stream. *Prepr Pap Am Chem Soc Div Fuel Chem*, 54(2), 954–955.

Svoboda, K., Lin, W., Hannes, J., Korbee, R., & van den Beek, C. M. (1994). Low temperature flue gas desulfurization by alumina-CaO regenerable sorbents. *Fuel*, 73(7), 1144–1150. doi:10.1016/0016-2361(94)90251-8

Terrones, M. (2003). Science and technology of twenty-five century: Synthesis, properties and applications. *Annual Review of Materials Research*, 33, 419. doi:10.1146/annurev.matsci.33.012802.100255

- Thess, A., Smalley, R. E., Roland, L., Nikolaev, P., Dai, H., & Petit, P. et al. (1996). Crystalline ropes of metallic carbon nanotubes. *Science*, 273(5274), 483–487. doi:10.1126/science.273.5274.483 PMID:8662534
- Velu, s., Ma, X., Song, C. (2003). Selective adsorption for removing sulfur from jet fuel over zeolite based adsorbents. *Industrial Engineering and Chemical Research*, 42(21), 5293–5304.
- Viculis, L. M., Mack, J. J., & Kaner, R. B. (2003, February 28). A chemical route to carbon nanoscrolls. *Science*, 299(5611), 1361. doi:10.1126/science.1078842 PMID:12610297
- Wang, Y. H., Yang, F. H., Yang, R. T., Heinzl, J. M., & Nickens, A. D. (2006). Desulfurization of high sulfur jet fuel by  $\pi$ -Complexation with copper and palladium halide sorbents. *Industrial & Engineering Chemistry Research*, 45(22), 7649–7655. doi:10.1021/ie060922w
- Wang, Y. H., Yang, R. T., & Heinzl, J. M. (2008). Desulfurization of jet fuel by  $\pi$ -complexation with metal halides supported on MCM-41 and SBA-15 mesoporous materials. *Chemical Engineering Science*, 63(2), 356–365. doi:10.1016/j.ces.2007.09.002
- Williams, G., Seger, B., & Kamat, P. V. (2008). TiO<sub>2</sub>-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano*, 2(7), 1487–1491. doi:10.1021/nn800251f PMID:19206319
- Xie, X., Ju, L., Feng, X., Sun, Y., Zhou, R., & Liu, K. et al. (2009). Controlled fabrication of high-quality carbon nanoscrolls from monolayer graphene. *Nano Letters*, 9(7), 2565–2570. doi:10.1021/nl900677y PMID:19499895
- Xue, Y. Z., Wu, B., Guo, Y. L., Huang, L. P., Jiang, L., & Chen, J. Y. et al. (2011). Synthesis of large-area, few-layer graphene on iron foil by chemical vapor deposition. *Nano Research*, 4(12), 1208–1214. doi:10.1007/s12274-011-0171-4
- Yang, F. H., Hernandez-Maldonado, A. J., & Yang, R. T. (2004). Selective adsorption of organosulfur compounds from transportation fuels by  $\pi$ -complexation. *Separation Science and Technology*, 39(8), 1717–1731. doi:10.1081/SS-120035937
- Yang, R. T. (2003). *Adsorbents: Fundamentals and Applications*. New York: Wiley. doi:10.1002/047144409X
- Yang, R. T., Hernandez-Maldonado, A. J., & Yang, F. H. (2003). Desulfurization of transportation fuels with zeolites under ambient conditions. *Science*, 301(5629), 79–81. doi:10.1126/science.1085088 PMID:12843388
- Yang, R. T., Takahashi, A., & Yang, F. H. (2001). New sorbents for desulfurization of liquid fuels by  $\pi$ -complexation. *Industrial & Engineering Chemistry Research*, 40(26), 6236–6239. doi:10.1021/ie010729w
- Yang, W., Ratnac, K. R., Ringer, S. P., Thordarson, P., Gooding, J. J., & Braet, F. (2010). Carbon nanomaterials in biosensors: Should you use nanotubes or graphene? *Angewandte Chemie International Edition*, 49(12), 2114–2138. doi:10.1002/anie.200903463 PMID:20187048
- Yang, X., Cao, C., Klabunde, K. J., Hohn, K. L., & Erickson, L. E. (2007). Adsorptive desulfurization with xerogel-derived zinc-based nanocrystalline aluminum oxide. *Industrial & Engineering Chemistry Research*, 46(14), 4819–4823. doi:10.1021/ie0701928

Yoshida, H., Shimizu, T., Uchiyama, T., Kohno, H., Homma, Y., & Takeda, S. (2009). Atomic-scale analysis on the role of molybdenum in iron-catalyzed carbon nanotube growth. *Nano Letters*, 9(11), 3810–3815. doi:10.1021/nl9019903 PMID:19731921

Yuan, L., Saito, K., Hu, W., & Chen, Z. (2001). Ethylene flame synthesis of well-aligned multi-walled carbon nanotubes. *Chemical Physics Letters*, 346(1-2), 23–28. doi:10.1016/S0009-2614(01)00959-9

Yudasaka, M., Komatsu, T., Ichihashi, T., & Iijima, S. (1997). Single wall carbon nanotube formation by laser ablation using double-targets of carbon and metal. *Chemical Physics Letters*, 278(1-3), 102–106. doi:10.1016/S0009-2614(97)00952-4

Zhang, Q., Huang, J. Q., Qian, W. Z., Zhang, Y. Y., & Wei, F. (2013). The Road for Nanomaterials Industry: A Review of Carbon Nanotube Production, Post-Treatment, and Bulk Applications for Composites and Energy Storage. *Small*, 9(8), 1237–1265. doi:10.1002/sml.201203252 PMID:23580370

Zhang, Q., Yu, Z., Du, P., & Su, C. (2010). Carbon nanomaterials used as conductive additives in lithium ion batteries. *Recent Patents on Nanotechnology*, 4(2), 100–110. doi:10.2174/187221010791208803 PMID:20415660

Zhou, H., Li, G., Wang, X., Jin, C., & Chen, Y. (2009). Preparation of a kind of mesoporous carbon and its performance in adsorptive desulfurization. *Journal of Natural Gas Chemistry*, 18(3), 365–368. doi:10.1016/S1003-9953(08)60117-6

Zhou, W. W., Han, Z. Y., Wang, J. Y., Zhang, Y., Jin, Z., & Sun, X. et al. (2006). Copper catalyzing growth of single-walled carbon nanotubes on substrates. *Nano Letters*, 6(12), 2987–2990. doi:10.1021/nl061871v PMID:17163745