

Chapter 4

Nanocomposites and Hybrid Materials for Adsorptive Desulfurization

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ABSTRACT

Desulfurization (removal of S compounds) of fuels is an important research topic in recent years. Several techniques have been reported to remove the sulfur-containing compounds in fuels. One of these techniques is adsorptive desulfurization (ADS) (removal based on chemisorption and physisorption) which has received much attention because of low energy consumption and facile operation condition. This chapter discusses the methods employed under this technique and the types of nanocomposites and hybrid materials (adsorbents) that have been investigated as potential adsorbents. The strategies to enhance sulfur adsorption capacity and main challenges will be discussed.

1. INTRODUCTION

Fossil fuels are the main source of energy worldwide; crude oil, which occurs naturally and comprises of several organic components (such as diesel, gasoline, jet fuels, kerosene etc.), serves as the major source of energy in the world. Crude oils are usually classified based on density and sulfur content. The lighter the crude oil the better its value and the lower the sulfur content in crude oil the better its profitability. Sulfur is the main important hetero-element found in crude oil and has the most significant effect on refining. It poisons catalyst, corrode refining equipment, and combustion of the products of sulfur from automobiles impair the emission control technology designed to meet the nitrogen oxides (NO_x) and

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particulate emission standards which leads to environmental pollution. It contributes to the deterioration of air quality and affects public health and the ecosystem. The maximum allowable sulfur content in highway diesel fuel in the US was 15 ppmw in 2006 and it will be less than 10 ppmw by 2017. Sulfur compounds found in crude oil are divided into aliphatic (mercaptans, sulfides, disulfides) and aromatic refractory group (thiophenes derivatives). The methods in use for the removal of sulfur compounds in fuels are either pre-combustion techniques or the post combustion techniques. The pre-combustion techniques are the best methods and they involve the decomposition of sulfur compounds, removal of the compounds without decomposition and final separation of the compounds followed by decomposition (Babich et al., 2003). The conventional method used by refineries for the removal of sulfur from the fuel is hydrodesulphurization (HDS) (Bej 2004). It is efficient in the removal of most aliphatic sulfur compounds from fuels e.g. thiols. However, it is not efficient in the removal of aromatic refractory sulfur compounds e.g. thiophene derivatives (dibenzothiophene (DBT) and 4, 6 dimethyl dibenzothiophene (DMDBT)) which are the least reactive and pose more serious danger to the environment. In addition, it requires high temperature, pressure and high dosage of catalyst before achieving the desired objective which is uneconomical (Ali et al., 2006).

Other methods of desulfurization in use to provide solutions to the problems of HDS include: Oxidative desulfurization (ODS), ionic liquids desulfurization (ILD) (Prashant et al., 2010), bio-desulfurization and ADS (Mohammad et al., 2006; Guoxian et al., 2005; Soleimani et al 2007; Isam et al., 2013; Celia et al., 2010). Most of these methods utilize a catalyst to speed up the rate of sulfur removal and they are considered viable alternatives in desulfurization. In ODS, all refractory sulfur compounds are oxidized by oxidants (such as H_2O_2 , H_2SO_4 , tBuOOH , O_3 and NO_2) to less harmful polar derivatives (sulfoxides and sulfones) that can be easily isolated by adsorption or extraction at room temperature and pressure. Most petroleum refineries use solvent extraction to extract the sulfur compounds from fuels, thereby recovering the solvent by distillation (Babich et al., 2003). The major disadvantages of ODS are: one, in appropriate oxidant may cause unwanted side reactions with other components in the fuel that are of interest and second, solvent selection is critical because undesirable solvents may extract other components of the fuel that will affect overall quality of the product. The use of IL in extractive and oxidative-extractive desulfurization started in 2001 (Bösmann et al., 2001) and it has become an area of interesting research since then. IL are organic salts composed of anions and cations and they have a low melting temperature. They are nonvolatile, nonflammable, chemically and thermally stable and they are easily regenerated due to their negligible vapor pressure. Different types of anions and cations have been used in this process such as: $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, alkylsulfates, thiocyanate or bis(trifluoromethylsulfonyl)imide, acetate, dialkylphosphate, alkylpyridinium, pyridinium, imidazolium, pyrrolidinium etc. Varying degrees of affinity and selectivity to sulfur compounds by different ionic IL have been noticed. Cost, lack of thermodynamic data, regeneration of the IL, effect of the liquids to other fuel constituents and corrosion related problems are the major drawbacks of this technology. (Zhang et al., 2002, 2004; Eber et al., 2004; Mochizuki et al., 2008; Cheruku et al., 2012; Holbrey et al., 2008; Borja et al., 2014). Biodesulfurization serves as an alternative to HDS due to its specificity, selectivity to sulfur compounds and mild operating conditions. In BDS, microbial species are used to consume sulfur compounds in fuels as their main energy source. They may either oxidize or reduce the sulfur compounds to sulfate or hydrogen sulfide respectively. Oxidizing the sulfur compounds is the most desirable pathway due to the fact that there will be no further treatment unlike the reduction pathway that requires further treatment of hydrogen sulfide through Claus process to elemental sulfur. Various strains of microbes have been studied to increase desulfurization activity such as: *Rhodococcus*, *desulfovibrio desulfuricans*, *Arthrobacter*, *Brevibacterium*

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