CHAPTER II
LITERATURE REVIEW

2.1 Transportation Fuels and Sulfur Compositions

2.1.1 Transportation Fuels

There are three major types of transportation fuels: gasoline, diesel, and jet fuel. The compositions of these fuels vary widely depending on the crude oil compositions, the refining process, the product demand, and the product specifications. The approximate compositions of gasoline, diesel, and jet fuel are given in Table 2.1. Branched and n-alkanes are the main ingredients of these fuels, typically 70-80%. The major alkanes in n-hexane and the main branched alkanes are C_5 and C_6 compounds. The aromatics are mainly benzene, toluene, xylenes and alkyl benzenes, totaling about 20-30%.

Table 2.1 Typical compositions of transportation fuels (vol%) (Yang, 2003)

	Gasoline[a]	Diesel[b]	Jet Fuel[c]
Boiling range (°C)	40-204	232-350	330-510
Aromatics	30.5	17	18
Olefins	1.8	5	2
n-alkanes	17.3	-	-
Branched alkanes	32	-	-
Cycloalkanes	5	-	-
Saturates	-	78	-
Paraffins	-	-	60
Naphthenes	-	-	20

[a]Sciences International, Inc., "Toxicological Profile for Gasoline," Report to Department of Health and Human Services, June, 1995.

[b]Ma *et al.*, 1994.

[c]Ma *et al.*, 2002.

2.1.2 Sulfur Compositions

Sulfur is a divalent element associated with hydrogen and carbon in 4 typed of principal compound: hydrogen sulfide, mercaptans, sulfides, and thiocyclic compounds (containing sulfur in a ring). The physical constants of the principal sulfur compounds are shown in Table 2.2.
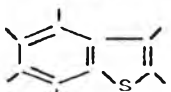
a. Hydrogen sulfide (H_2S) is not found in petroleum products but it does exist in small amounts in crude oils and in varying amounts in natural gas. It is also present in large quantities in the refinery as many units generate H_2S as compulsory step in the desulfurization process. Refineries therefore have to handle and process large quantities of H_2S and have to apply extremely strict safety regulations as it is a very toxic and dangerous gas. It is also corrosive, particularly at low temperature when dissolved in water where it breaks down into sulfuric acid.

b. Mercaptans are composed of the functional combination associated with a hydrocarbon chain represented by the letter R. Mercaptans occur in most petroleum cuts and they have the following drawbacks: acid and obnoxious smell. Refinery installations therefore generally have to include equipment for removing these compounds.

c. Sulfides are that the sulfur atoms are linked to two hydrocarbon chains. The sulfur therefore forms an intermediary between the two chains and a distraction is made between sulfides, disulfides or polysulfides. These compounds occur in crude oils and petroleum products. Unlike mercaptans, they have the advantage of not being acid which means they are not corrosive and their low volatility greatly reduces their smell.

d. Thiocyclic compounds are the most commonly found in crude oils and petroleum products and chiefly derived from thiophene and benzothiophene. Their characteristics are similar to those of aromatic hydrocarbons: unsaturated rings and good thermal stability, they are neutral and non-corrosive. The desulfurization of petroleum products consists in destroying these compounds, which is not an easy task, particularly in the case of very heavy thiophenic compounds.

Table 2.2 Typical organic sulfur compounds

	Chemical formula	Structural formula	Molecular weight	Normal boiling point °C	Sp gr [15] (liquid)
hydrogen sulfide	H_2S	H – S – H	34.1	– 60.3	
MERCAPTANS					
methylmercaptan	CH_3SH	– C – S – H	48.1	6.0	0.873
ethylmercaptan	C_2H_5SH	– C – C – S – H	62.1	35.0	0.845
n-propylmercaptan	C_3H_7SH	– C – C – C – S – H	76.2	67.6	0.847
n-butylmercaptan	C_4H_9SH	– C – C – C – C – S – H	90.2	98.5	0.847
SULFIDES					.
dimethylsulfide	C_2H_6S	– C – S – C –	62.1	37.3	0.854
ethylmethylsulfide	C_3H_8S	– C – S – C – C –	76.2	66.6	0.848
diethylsulfide	$C_4H_{10}S$	– C – C – S – C – C –	90.2	92.1	0.841
methyl n-propylsulfide	$C_4H_{10}S$	– C – S – C – C – C –	90.2	95.5	0.847
DISULFIDES					
dimethyldisulfide	C_2H_6S	– C – S – S – C –	94.2	109.6	1.069
diethyldisulfide	$C_4H_{10}S_2$	– C – C – S – S – C – C	122.2	152.6	0.998
dipropyldisulfide	$C_6H_{14}S_2$	– C – C – C – S – S – C – C – C –	150.3	126.5 at 100mm of Hg	0.964
THIOPHENIC COMPOUD					
thiophene	C_4H_4S	(ring structure)	84.1	84	1.070
methylthiophene	$CH_3C_4H_3S$	(ring structure)	98.2	119	1.069
benzothiophene	C_8H_6S	(ring structure)	134.2	220	1.165

The sulfur compounds in transportation fuels can be analyzed with X-ray fluorescence spectroscopy or by gas chromatography equipped with a capillary column plus flame photometric detector. The remaining sulfur compounds after hydrodesulfurization (HDS) are mainly thiophene (T), benzothiophene (BT),

dibenzothiophene (DBT) and their alkylated derivatives. The alkylated derivatives with alkyl groups at the 4- and 6-positions are the most difficult to remove and are referred to as refractory species. Ma *et al.*, (2002) showed GC-FPD chromatograms of a sample each of gasoline, diesel, and jet fuel in Figure 2.1. The FPD detects only sulfur compounds. The dominant sulfur compounds in the gasoline were (in decreasing order) 3-MT, BT, T, 2-MT, and 2,4-DMT. No mercaptans, dialkyl sulfides and dialkyl disulfides were detected. Those in the diesel were 4-MDBT, 4,6-DMCBT, 2,4,6-TMDBT, 3,6-DMDBT, DBT, 2,3,7-TMBT, 2,3,5-TMBT, 2,3-DMBT, and others. The sulfur compounds in the jet fuel were 2,3,7-TMBT, 2,3-DMBT, and the minor species 2,3,5-TMBT and 2,3,6-TMBT. All these MBT have two methyl groups at 2- and 3-positions, respectively, implying that the BT with two methyl groups at 2- and 3-positions are more difficult to be removed than other sulfur compounds in hydrotreating of jet fuel.
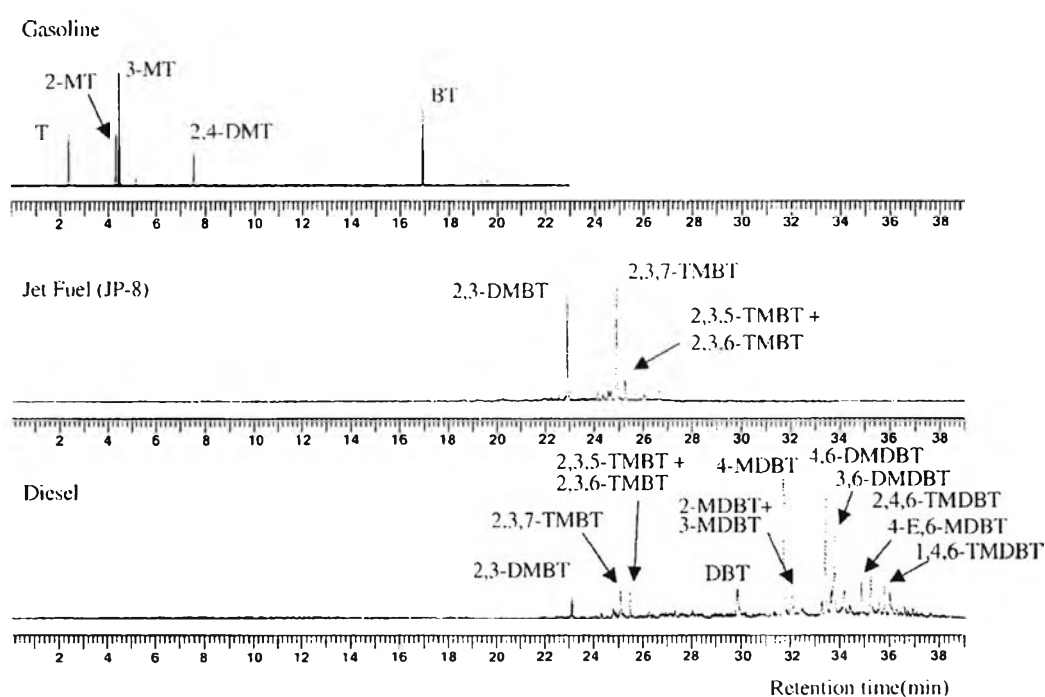
Figure 2.1 GC-FPD chromatograms of gasoline, jet fuel and diesel for identification of sulfur compounds (Ma *et al.*, 2002).

2.2 Sulfur Removal Processes

There are several processes that can remove organic sulfur from fuels to desired levels. But there is no universal approach to classify desulfurization processed. The processes can be categorized by the fate of the organic sulfur compounds during desulfurization, the role of hydrogen, or the nature of the process used (chemical and/or physical) (Babich *et al.*, 2003). One way of the Babich's classifications is based on the nature of the key physico-chemical process used for sulfur removal (Figure 2.2). The most developed and commercialized technologies are those which catalytically convert organic sulfur compounds with sulfur elimination. Such catalytic conversion technologies include conventional hydrotreating, hydrotreating with advanced catalysts and/or reactor design, and combination of hydrotreating with some additional chemical processes to maintain fuel specifications. The main feature of the technologies of the second type is the application of physico-chemical processes different in nature from catalytic HDS to separate and/or to transform organic sulfur compounds from refinery streams. Such technologies include as a key step distillation, alkylation, oxidation, extraction, adsorption or combination of these processed.
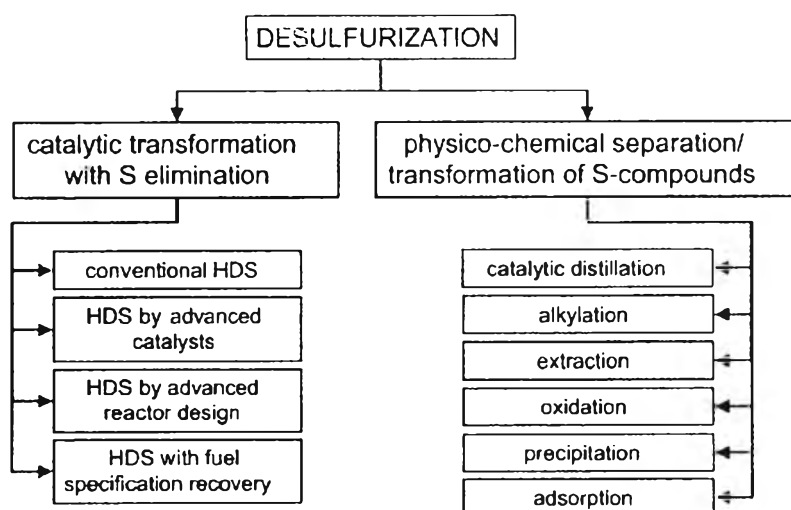
Figure 2.2 Desulfurization technologies classified by nature of a key process to remove sulfur (Babich *et al.*, 2003).
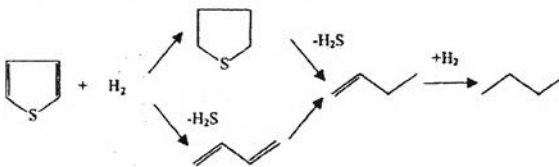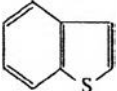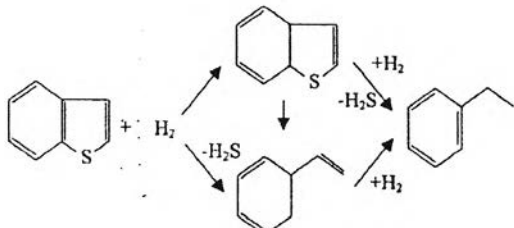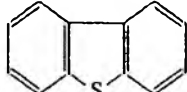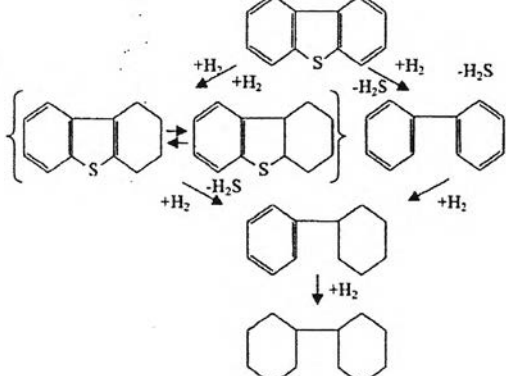
2.2.1 Conventional Hydrodesulfurization (HDS)

The hydrodesulfurization process involves catalytic treatment with hydrogen to convert the various sulfur compounds present to hydrogen sulfide. The hydrogen sulfide is then separated and converted to elemental sulfur by the Claus process. From this point, some of the hydrogen sulfide is oxidized to sulfur dioxide by air and sulfur is formed by the overall reaction:

$$2H_2S + SO_2 \longrightarrow 3S(s) + 2H_2O$$
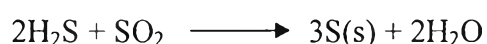
The conventional HDS process is usually conducted over sulfided Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 catalyst under high temperature (300-340 °C) and high pressure (20-100 atm of H_2). Their performance in terms of desulfurization level, activity and selectivity depends on the properties of the specific catalyst used (active species concentration, support properties, synthesis route), the reaction conditions (sulfiding protocol, temperature, partial pressure of hydrogen and H_2S), nature and concentration of sulfur compounds present in the feed stream, and reactor and process design (Babich *et al.*, 2003). However, these catalysts are poisoned by H_2S and metals in feedstock. There is generally no method for regeneration other than running straight hydrogen through the reactor.

The reactivity of organic sulfur compounds varies widely depending on their structure and local sulfur atom environment. The low-boiling crude oil fraction contains mainly the aliphatic organic sulfur compounds: mercaptans, sulfides and disulfides. They are very reactive in conventional hydrotreating processes and they can easily be completely removed from the fuel. For high boiling crude oil fractions, the organic sulfur compounds pre-dominantly contain thiophenic rings. These compounds include thiophenes and benzothiophenes and their alkylated derivatives. These thiophene containing compounds are more difficult than mercaptans and sulfides to convert via hydrotreating. The organic sulfur compounds and their hydrotreating pathway are shown in Table 2.3.

Table 2.3 The organic sulfur compounds and their hydrotreating pathway (Babich *et al.*, 2003)

Typical organosulfur compounds and their hydrotreating pathway

Type of organic sulfur compound	Chemical structure	Mechanism of hydrotreating reaction[a]
Mercaptanes	$R-S-H$	$R-S-H + H_2 \rightarrow R-H + H_2S$
Sulfides	R^1-S-R^2	$R^1-S-R^2 + H_2 \rightarrow R^1-H + R^2-H + H_2S$
Disulfides	$R^1-S-S-R^2$	$R^1-S-S-R^2 + H_2 \rightarrow R^1-H + R^2-H + H_2S$
Thiophene		
Benzothiophene		
Dibenzothiophene		

[a] Reaction pathway for alkylated thiophene, benzothiophene and dibenzothiophene is similar to the reaction of nonalkylated counterparts.

2.2.2 Desulfurization by Adsorption

Adsorption processes consist of the selective concentration of one or more components of either a gas or a liquid at the surface of a solid (adsorbent). The attractive forces causing the adsorption are generally weaker than those of chemical bonds, and by increasing the temperature of the adsorbent or reducing an adsorbate's partial pressure (or concentration in a liquid), the adsorbate can be desorbed (Rousseau, 1987).

There are two types of adsorption: physical adsorption and chemisorption. The physical adsorption involves only relatively weak intermolecular forces. These forces include van de Waals forces (dispersion-repulsion) and electrostatic interactions comprising polarization, dipole, and quadrupole interactions. The chemisorption involves, essentially, the formation of chemical bond between the sorbate molecule and the surface of the adsorbent (Ruthven, 1984).

Adsorptive separation is achieved by one of three mechanisms: steric, kinetic, or equilibrium effect. The steric effect derives from the molecular sieving properties of zeolites and molecular sieves. In this case only small and properly shaped molecules can diffuse into the adsorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the differences in diffusion rates of different molecule. A large majority of processes operate through the equilibrium adsorption of mixture and hence are called equilibrium separation processes (Yang, 2003).

Desulfurization by adsorption is based on the ability of a solid sorbent to selectively adsorb organic sulfur compounds from refinery steams. Based on the mechanism of the sulfur compound interaction with the sorbent, desulfurization by adsorption can be divided into two groups: adsorptive desulfurization and reactive adsorptive desulfurization. Adsorptive desulfurization is based on physical adsorption of organic sulfur compounds on the solid sorbent surface. Regeneration of the sorbent is usually done by flushing the spent sorbent with a desorbent, resulting in a high organic sulfur compound concentration flow. Reactive adsorption desulfurization employs chemical interaction of the organic sulfur compounds and the sorbent. Sulfur is fixed in the sorbent, usually as sulfide, and the S-free hydrocarbon is released into purified fuel stream. Regeneration of the spent sorbent results in sulfur elimination as H_2S, S, or SO_x, depending on the process applied. Efficiency of the desulfurization is mainly determined by the sorbent properties: its adsorption capacity, selectivity for the organic sulfur compounds, durability and regenerability (Babich *et al.*, 2003).

2.3 Adsorbents for Sulfur Removal

2.3.1 Types of Adsorbent

Commercial adsorbents are divided into four major types: activated carbon, molecular –sieve zeolites, silica gel, and activated alumina. Since adsorption is a surface-related phenomenon, the useful adsorbents are all characterized by large surface area per unit of weight (or volume). The typical range of areas covers from about 100 to over 3000 m^2/g. However, the most common commercially useful materials exhibit surface areas ranging from about 300 to 1200 m^2/g (Rousseau, 1987).

2.3.1.1 Activated Carbons

Activated carbon is a microcrystalline, nongraphitic form of carbon that has been processed to develop internal porosity. Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature (700-1000°C). The structures of activated carbon are stacked together in random orientation and it is the spaces between the crystals which form the micropores. The porosity yields the surface area that provides for the ability to adsorb gases and vapors from gases, and dissolved or dispersed substances from liquids. The actual distribution and the total pore volume associated with each pore size range are however sensitive to the conditions of the initial pyrolisis and activation procedures. Typical ranges are given in Table 2.4. but by special procedures it is possible to prepare activated carbons with even higher porosity, surface area, and adsorptive capacity.

The surface of carbon is essentially non polar although a slight polarity may arise from surface oxidation. As a result, carbon adsorbents tend to be hydrophobic and organophillic. They are therefore widely used for the adsorption of organics in decolorizing sugar, water purification, and solvent recovery systems as well as for the adsorption of gasoline vapors in automobiles and as a general purpose adsorbent in range hoods and other air purification systems. In order to decrease the mass transfer resistance, the activated carbons used for adsorption from the liquid phase generally have somewhat larger pore diameters than those used for adsorption from the gas phase (Ruthven, 1984; Rousseau, 1987).

Table 2.4 Pore sizes in typical activated carbon (Ruthven, 1984)

	Micropore	Mesopore or Transitional Pores	Macropores
Diameter (Å)	< 20	20-500	>500
Pore volume (cm^3/g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area (m^2/g)	100-1000	10-100	0.5-2
(Particle density 0.6-0.9 g/cm^3; porosity 0.4-0.6)			

2.3.1.2 Molecular-Sieve Zeolites

Molecular-sieve zeolites are porous crystalline aluminosilicates. The structure of zeolites consists of a three-dimensional framework of SiO$_4$ and AlO$_4$ tetrahedra, each of which contains silicon or aluminum atom in the canter. The oxygen atoms are shared between adjoining tetrahedral, which can be present in various ratios and arranged in a variety of ways. Molecular-sieve zeolites may be represented by the empirical formula:
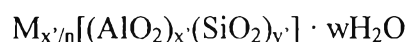
$$M_{2/n} \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$
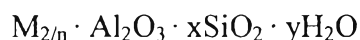
where x is 2 or greater, n is the cation valence, and y represents the water contained in the voids of the zeolite. Zeolites are also represented by a structure formula that based on the crystal unit cell, the smallest unit of structure

$$M_{x'/n}[(AlO_2)_{x'}(SiO_2)_{y'}] \cdot wH_2O$$

where n is the valence of cation M, w is the number of water molecules per unit cell, x' and y' are the total number of tetrahedral per unit cell, and x'/y' usually has values of 1-5.

The zeolites of most interest in catalysis are those having medium to large pore sizes, consisting of 10- or 12-ring oxygen atoms, and having relatively high Si/Al ratios. The latter may stem from the initial synthesis method or from subsequent treatments. Zeolites of high current interest industrially include

zeolite Y and mordenite, which have a 12-ring system, and zeolite ZSM-5, which has a 10-ring system. Some structural information in these and other zeolites of particular interest in catalysis is given in Table 2.5 (Ruthven, 1984; Rousseau, 1987).

Table 2.5 Selected well-characterized zeolites of interest in catalysis (Satterfield, 1991)

| Number of O atoms in the larger aperture ring	Channel geometry (nm)	Secondary building unit (sbu)	Structure type
Mordenite	One-dimensional tube 0.65 x 0.70 interconnecting with an 8-ring pore structure 0.29 x 0.57, one-dimensional	5-1	MOR
Faujasite (zeolite X, Y, LZ-210)	Three-dimensional, with 0.74 aperture, leading to 1.2 diameter cavities	D6R	FAU
Offretite (zeolite O, LZ-217)	0.64 one dimensional with cavities, interconnecting with a 2-dimensional 8-ring system consisting of 0.36 x 0.49 channels. Overall, a 3-dimensional system.	S6R	OFF
Linde type L (in K-form)	One-dimensional, 0.71 aperture, 0.48 x 1.24 x 1.07	S6R	LTL
Mazzite (ZSM-4, Ω LZ-202)	One-dimensional, nearly cylindrical channels 0.74 diameter, separated from one-dimensional 8 ring channels, 0.34 x 0.56	5-1	MAZ
Zeolite β (Nu-2)	Three-dimensional network		

Table 2.5 (cont.) Selected well-characterized zeolites of interest in catalysis (Satterfield, 1991)

Number of O atoms in the larger aperture ring	Channel geometry (nm)	Secondary building unit (sbu)	Structure type
Zeolite ZSM-5	Two-dimensional, 0.51 x 0.55 tube interconnecting with zigzag 0.53 x 0.56 tube	5-1	MFI
ZSM-11	Two-dimensional, interconnecting tubes, 0.53 x 0.54	5-1	MEL
Ferrierite (ZSM-35)	Two-dimensional interconnecting network of 10- and 8-ring pores 0.54 x 0.42 and 0.48 x 0.35	5-1	FER
Erionite	0.36 x 0.51 (tortuous), three-dimensional	S6R	ERI
Linde A	Three-dimensional, 0.41		

2.3.1.3 Silica Gel

Silica gel is a partially dehydrated form of polymeric colloidal silicic acid. The chemical composition can be expressed as $SiO_2 \cdot nH_2O$. The water content, which is present mainly in the form of chemically bound hydroxyl groups, amounts typically to about 5 wt.% (Ruthven, 1984). The commercial silica gel sorbents are mesoporous, that is, with pores mostly larger that 20 Å. Silica gel can be formed by two routs: (1) polymerization of silicic acid, and (2) aggregation of particles of colloidal silica. Silicic acid, $Si(OH)_4$, has a strong tendency to polymerize and form a network of siloxane (Si-O-Si) as Figure 2.3, leaving a minimum number of uncondensed Si-O-H groups. The pH value is important in the polymerization process. The second route involves coagulation of silica sols of rather uniform sizes. These submicrometer particles can coagulate by van der Walls forces or by cations bridging as coagulants. Commercially, silica is prepared through the first route by

mixing a sodium silicate solution with a mineral acid, such as sulfuric acid or hydrochloric acid.

$$\begin{array}{c} /\overset{O}{\diagup}\backslash \\ -\!\!-\text{Si}-\!\!-\text{Si}-\!\!- \\ | \qquad | \end{array}$$
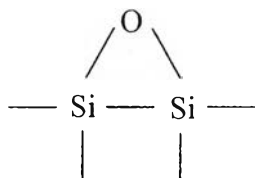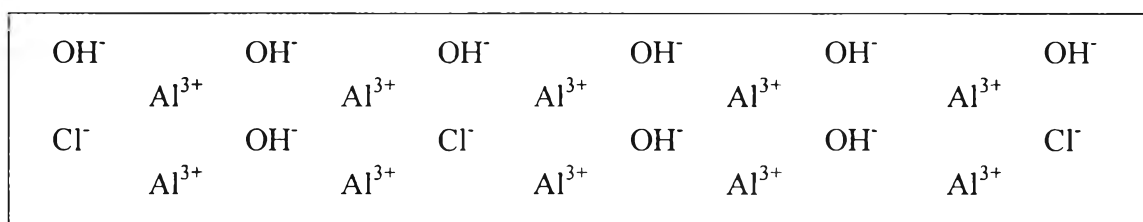
Figure 2.3 Siloxane group (Satterfield, 1991).

The most-used property for silica gel is as a desiccant, that is, adsorbent for moisture. As mentioned, this quality is due to its relatively weak bonds with water as well as its large pore volume and mesoporosity (Yang, 2003).

2.3.1.4 Activated Alumina

Activated alumina is a porous high-area form of aluminum oxide, prepared either directly from bauxite ($Al_2O_3\cdot3H_2O$) or from the monohydrate by dehydration and recrystallzation at elevated temperature. The surface area is more strongly polar than that of silica gel and has both acidic and basic character, reflecting the amphoteric nature of the metal (Ruthven, 1984). The surface acidity is the most important property for both adsorption and catalysis. Unlike silica, Lewis acid sites are usually abundant on aluminas. These are the Al^{3+} sites on the surfaces. There are both tetrahedral and octahedral Al^{3+} sites. The acidity of the surface can be increased with acid, such as HCl and HF. Partial conversion of a fully hydrate alumina surface by the acid treatment would form a surface that contains both Cl^- and OH^- groups:

OH^-		OH^-		OH^-		OH^-		OH^-		OH^-
	Al^{3+}		Al^{3+}		Al^{3+}		Al^{3+}		Al^{3+}	
Cl^-		OH^-		Cl^-		OH^-		OH^-		Cl^-
	Al^{3+}		Al^{3+}		Al^{3+}		Al^{3+}		Al^{3+}	

Activated alumina is a versatile sorbent that can be tailored for many special applications. New applications continue to be developed, mainly by

aluminum companies. The following are proven applications of various tailored aluminas (Yang, 2003):

- Removal of HCl and HF from gases and liquids
- Removal of acidic gases (COS, CO_2, H_2S, CS_2) from hydrocarbons
- Removal of oxygenates and Lewis Bases
- Removal of polar organic compounds
- Removal of As^{5+}, PO_4^{3-}, Cl^-, and F^- from water
- Scavenger for organic process liquids
- Alkalized alumina for SO_2 removal

2.3.2 Types of Metal Loading on Adsorbent

In a past few years, there were a lot of researches which concentrated on the removal of sulfur compounds from transportation fuels by using various types of metals. There are two major types of oxidation number that are usually used: 1^+ and 2^+. These metals can increase the capacity and selectivity of the adsorption of organic sulfur compounds.

For the 1^+ oxidation numbers, such as Ag^+ and Cu^+ were studied by many researchers. For example, Yang *et al.* (2001) studied Cu(I)-Y and Ag-Y as selective sorbents for desulfurization of liquid fuels. Thiophene and benzene were used as the model system and vapor-phase isotherms were measured. The results show that Cu(I)-Y and Ag-Y adsorbed significantly larger amounts of both thiophene and benzene at low pressures as a result of π-complexation with Cu^+ and Ag^+. On a per-cation basis, more thiophene was adsorbed by Cu^+ than by Ag^+. Hernández-Maldonado *et al.* (2004) studied the desulfurization of a commercial diesel fuel by used different adsorbents with Cu(I) in a fixed-bed adsorber operated at ambient temperature and pressure. They observed that the adsorbents tested for total sulfur adsorption capacity at breakthrough followed the order: AC/Cu(I)-Y > Cu(I)-Y > Selexsorb$^@$ CDX (alumina) > CuCl/γ-Al_2O_3 > activated carbon > Cu(I)-ZSM-5.

The 2^+ oxidation numbers, Ni^{2+}, Cu^{2+}, Fe^{2+}, and Zn^{2+} can be also used. For example, Hernández-Maldonado *et al.* (2004) studied the desulfurization of a

commercial diesel fuel by different Ni(II)-exchanged faujasite zeolites. The results show that the adsorbents tested for total sulfur adsorption capacity at breakthrough followed the order: Selexsorb CDX (alumina)/Ni(II)-Y (SSIE-500) > Selexsorb CDX (alumina)/Ni(II)-X (LPIE-RT) > Ni(II)-Y (SSIE-500) > Ni(II)-X (LPIE-RT) > Ni(II)-Y (LPIE-135). King et al. (2006) studied the desulfurization of gasoline by divalent copper-exchanged zeolite Y (Cu(II)-Y) zeolite. Sulfur removal was found to be greater at 150 °C than at lower temperature for Cu(II)-Y adsorbents containing as the secondary cation either Na^+ (CuNaY) or H^+ (CuHY). Overall, the CuHY zeolite showed somewhat better desulfurization performance. Bhandari et al. (2006) studied on sulfur removal to acceptable levels by using adsorption process at room temperature. They used Y-zeolites, ion exchanged with metal ions that are capable of π-complexation. A very high sulfur removal capacity has been observed for Ni-Y (~42 mg/g) and Cu-Y (~31 mg/g) zeolites. These along with other ion exchange zeolites such as Fe-Y and Zn-Y have been found to effectively remove sulfur from commercial diesel, although the capacity in the later case was lower than that observed with model diesel. Zhang et al. (2008) studied the adsorptive removal of organic sulfur compounds including dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) on various ion exchanged Na-Y zeolites with single Cu^{2+}, Zn^{2+}, Ag^+ and the combined Cu^{2+}-Zn^{2+}, Zn^{2+}-Nd^{3+}, Ni^{2+}-Nd^{3+} in model systems. It was observed that the desulfurization efficiency follows the order of direct adsorption > oxidation-adsorption > direct-oxidation. The Ag-Y and CuZn-Y are very capable of removing DBT and 4,6-DMDBT adsorption approach. The co-exchanged CuZn-Y adsorbent is a promising competitor to Ag-Y according to deep desulfurization performance for DBT and 4,6-DMDBT as well as the higher stability of adsorbent.

Moreover 3^+ oxidation number can be used, such as Ce^{3+}. Xue et al. (2005) observed the adsorption of thiophene and 1-benzothiophene in model gasoline using NaY-zeolites exchanged with Ag^+, Cu^{2+}, and Ce^{3+} ions and NH_4Y-zeolites exchanged with Ce^{3+} ions. The results show that the sulfur uptake increased in the order CuY-zeolite(Na) < AgY-zeolites(Na) < CeY-zeolite(Na) for both the organic sulfur compounds. CeY-zeolite(NH_4) which was prepared from NH_4Y-zeolite

showed less uptake thiophene and 1-benzothiphene than CeY-zeolite(Na) probably due to its lower cerium content.

2.3.3 Adsorbent Preparation

2.3.3.1 Precipitation and Coprecipitation

The preparation of catalysts and supports by precipitation or coprecipitation is technically very important. However, precipitation is usually more demanding than several other preparation techniques, due to the necessity of product separation after precipitation and the large volumes of salt-containing solutions generated in precipitation processes. On other systems precipitation techniques are also used, for instance in the production of iron oxides, titanium oxides or zirconias. The main advantages of precipitation for the preparation of such materials are the possibility of creating very pure materials and the flexibility of the process with respect to final product quality.

Other catalysts, based on more than one component, can be prepared by coprecipitation. According to IUPAC nomenclature, coprecipitation is the simultaneous precipitation of normally soluble component with a macrocomponent from the same solution by formation of mixed crystal, by adsorption, occlusion or mechanical entrapment. However, in catalyst preparation technology, the term is usually used in a more general sense in that the requirement of one species being soluble is dropped. In many cases, both components to be precipitated are essentially insoluble under precipitation conditions, although their solubility products might differ substantially. We will therefore use the term coprecipitation for the simultaneous precipitation of more than one component. Coprecipitation is very suitable for the generation of a homogeneous distribution of catalyst components or for the creation of precursors with definite stoichiometry, which can be easily converted to the active catalyst. Such a good dispersion of catalyst components is difficult to achieve by other means of preparation, thus coprecipitation will remain an important technique in the manufacture of heterogeneous catalysts in spite of the disadvantages associated with such processed. These disadvantages are the higher technological demands, the difficulties in following the quality of the precipitated product during the precipitation, and the problem in maintaining a constant product quality throughout the whole precipitation

process, if the precipitation is carried out discontinuously. Table 2.6 gives an overview of industrially used precipitated catalysts and supports.

Table 2.6 Some industrially relevant catalysts and supports obtained by precipitation or coprecipitation techniques (Ertl *et al.*, 1997)

Material	Use	Important examples
Al_2O_3 (mostly γ, in special cases α or η)	support, catalyst	Clause process, dehydration of alcohols to alkene and ethers, support of hydrotreating catalysts, support for three-way catalyst
SiO_2	support	noble metal/SiO_2 for hydrogenation reactions, Ni/SiO_2 for hydrogenation reactions, V_2O_5/SiO_2 for sulfuric acid production
Al_2O_3/SiO_2	catalyst	acid-catalyzed reactions such as isomerizations
Fe_2O_3	catalyst, catalyst component	Fischer-Tropsch reactions, major component of catalyst for ethylbenzene reaction to styrene
TiO_2	support, catalyst, catalyst component	major component of DeNOx catalyst
ZrO_2	catalyst	acid catalyst after sulfate modification
Cu/ZnO	catalyst	methanol synthesis
$(VO)_2P_2O_7$	catalyst	selective oxidation – for instance butane to maleic anhydride

Table 2.6 (cont.) Some industrially relevant catalysts and supports obtained by precipitation or coprecipitation techniques (Ertl *et al.*, 1997)

Material	Use	Important examples
Cu – Cr oxides	catalyst	combustion reactions, hydrogenations
AlPO4	support, catalyst	polymerization, acid-catalyzed reactions
Sn – Sb oxide	catalyst	selective oxidation – for instance isobutene to methacrolein
Bi molybdates	catalyst	selective oxidation – for instance propene to acrolein (mostly supported)
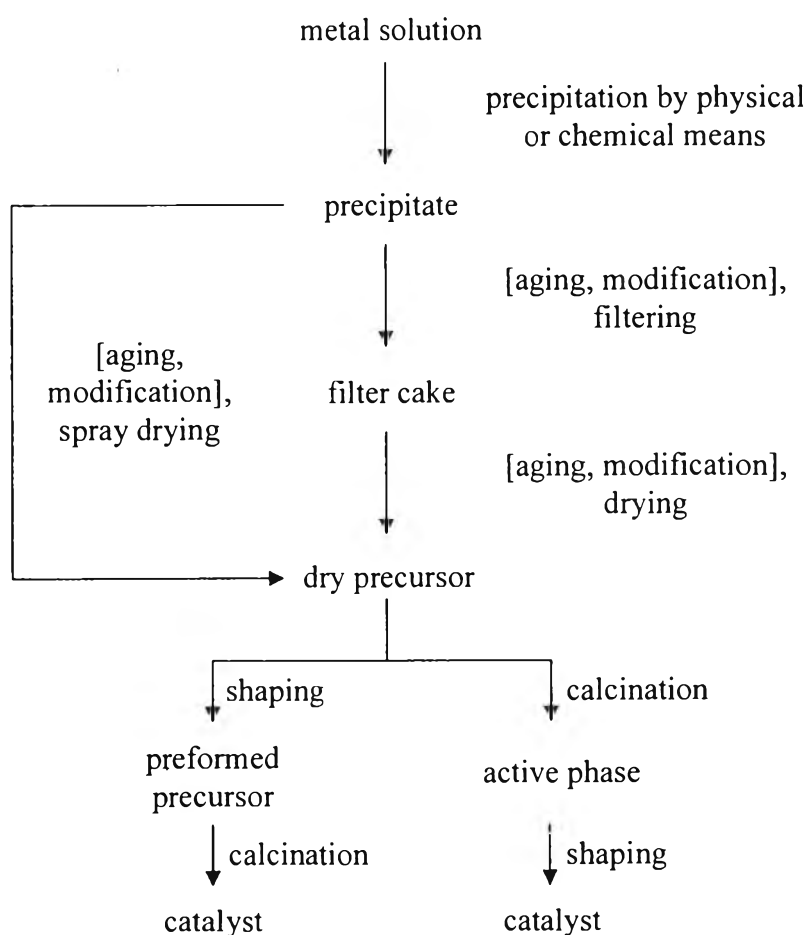
Figure 2.4 Preparation scheme for precipitated catalyst. Optional preparation steps are indicated by square brackets (Ertl *et al.*, 1997).
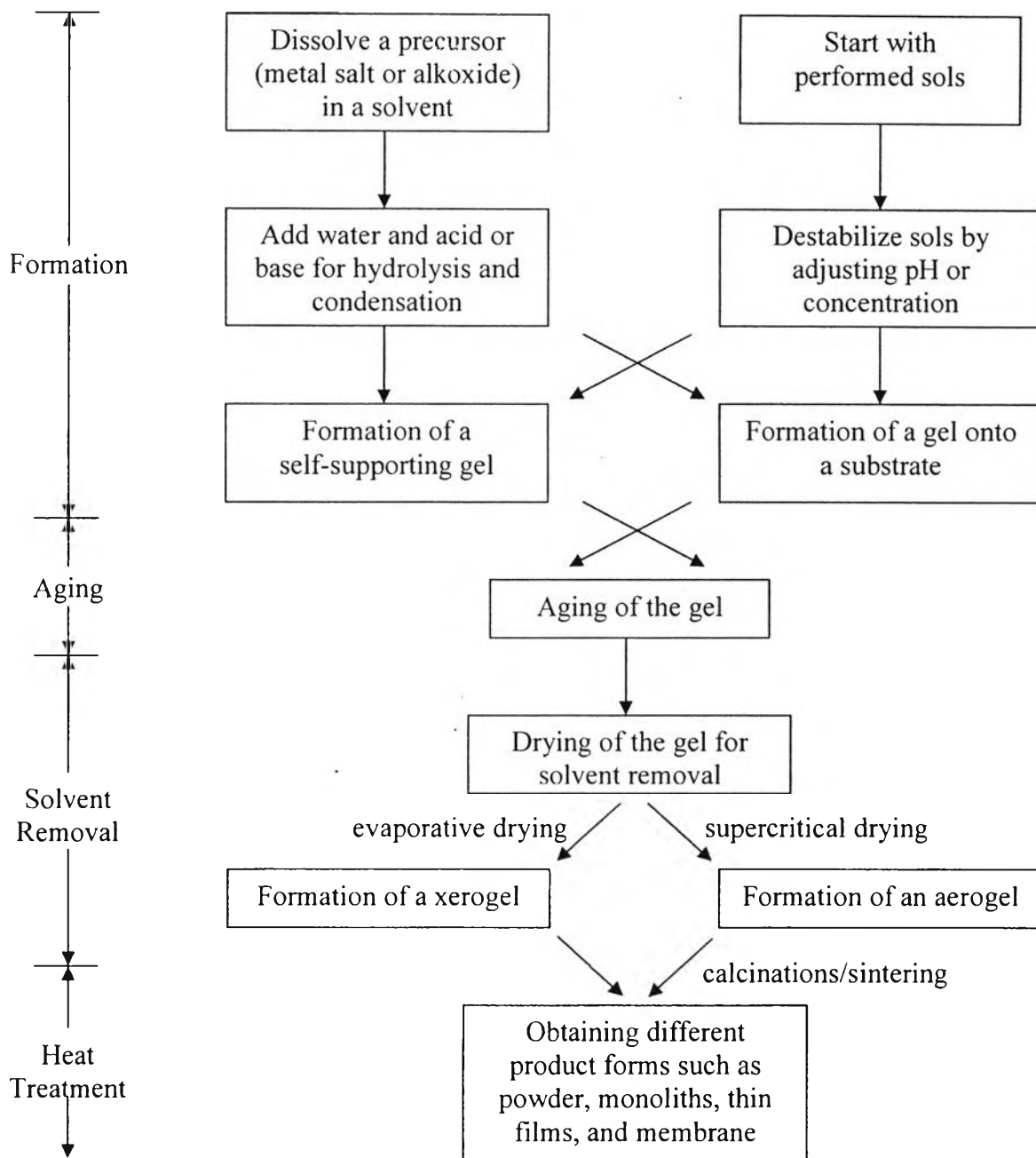
The investigations of crystallization and precipitation processes from solution often have to rely on indirect and theoretical methods. Figure 2.4 depicts a general flow scheme for the preparation of a precipitation catalyst.

2.3.3.2 Sol–Gel Process

The sol–gel process involves first the formation of a sol followed by that of a gel. A sol, which is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron, can be obtained by the hydrolysis and partial condensation of precursor such as an inorganic salt or a metal alkoxide. The further condensation of sol particles into a three-dimension network produces a gel, which is a diphasic material with a solid encapsulating a solvent. Alternatively, a gel can be produced by destabilizing a solution of performed sols. In either case the materials are refereed to aquasol (or aquagel) when water is used as a solvent, and alcosol (or alcogel) when alcohol is used. The encapsulated liquid can be removed from a gel by either evaporative drying or drying with supercritical extraction. The resulting solid products are known as xerogel and an aerogel, respectively. The single most important characteristic of the sol–gel preparation of catalytic materials in its ease of control that translates into the following advantages:

- The ability to maintain high purity (because of purity of staring materials)
- The ability to change physical characteristics such as pore size distribution and pore volume
- The ability to vary compositional homogeneity at a molecular level
- The ability to prepare samples at low temperatures
- The ability to introduce several components in a single step
- The ability to produce samples in different physical forms

Figure 2.5 shows the four key steps in taking a precursor to a particular product form via sol–gel preparation: formation of gel, aging of gel, removal of solvent, and heat treatment.

Dissolve a precursor (metal salt or alkoxide) in a solvent		Start with performed sols

Formation

Add water and acid or base for hydrolysis and condensation		Destabilize sols by adjusting pH or concentration

Formation of a self-supporting gel		Formation of a gel onto a substrate

Aging

Aging of the gel

Solvent Removal

Drying of the gel for solvent removal

evaporative drying   supercritical drying

Formation of a xerogel	Formation of an aerogel

calcinations/sintering

Heat Treatment

Obtaining different product forms such as powder, monoliths, thin films, and membrane

Figure 2.5 Schematic diagram showing the various steps of a sol–gel process (Ertl *et al.*, 1997).

2.3.3.3 Ion Exchange

Ion exchange consists of replacing an ion in an electrostatic interaction with the surface of a support by another ion species. The support containing ion A is plunged into an excess volume (compared to the pore volume) of a solution containing ion B that is to be introduced. Ion B gradually penetrates into the pore space of the support and takes the place of ion A, which passes into the solution, until equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution.

Almost all solid mineral supports are oxides. They behave like ion exchangers when their surface bears electric charges. Two categories may be distinguished: natural exchangers which are composed of framework bearing electric charges neutralized by ions of opposite sign and amphoteric oxides (Ertl *et al.*, 1997).

2.3.3.4 Impregnation

Preparation of impregnated catalysts usually involves filling the pore structure of shaped, porous support body with a solution of catalyst component(s), removing the solvent, and activating the catalyst. The impregnating solution may be a simple water solution of one or more soluble salts of the metal(s) and counterions to be deposited, or it may be a complex mixture incorporating solubilizing agents and/or reactants, such as reducing agents that function during as activation step.

In the so-called dry impregnation method, the amount of solution added to the solid support is exactly that calculated to completely fill the pores of the support. The solution may be sprayed into the support in blending operation and usually is adsorbed quickly because of capillary action. The resulting mixture appears dry to the eye, thus the name dry impregnation has been applied. This method works well with supports that have relatively large, open-ended pores, even with aqueous solutions having a relatively high surface tension. Careful attention must be paid to the viscosity of the solution, which affects how much solution can be absorbed by the solid. Certain hydrotreating catalysts containing transition metals on alumina are examples of the use of this manufacturing method.

For catalyst supports with extremely small pores or a closed-end pore structure, it may be difficult to fill the support completely with impregnating solution by the dry impregnation method. In this case, immersion of the support in a solution containing the catalytically active components usually is more effective. Unless the solvent used has a high vapor pressure or contains dissolved gases, a complete pore volume impregnation usually can be aided by the use of vacuum. In this case, the bare support is placed in suitable vessel, the air is withdrawn, and sufficient solution is introduced to cover the support while it is under vacuum. Air, or in some cases another gas, is then admitted to the vessel until at least atmospheric pressure is established, which forces the liquid into the evacuated pore structure of the support. Excess liquid is drained from the wet support and the excess solution is discharged. Liquids are removed from the impregnated support by controlled heating with or without the use of reduced pressure. Depending on the nature of the finished catalyst, the impregnated support may or may not be treated further or calcined in subsequent steps (Grant, 1992).

2.3.4 Cu Impregnations

It has been known for a long time that metal oxides and salts can be dispersed on solid subtrates in a monolayer form, that is, as opposed to form a stoichiometric compound with the support, or to be dissolved in the support to form a solid solution. One of two general approaches for making a monolayer or near-monolayer salts dispersion on porous supports is the incipient wetness impregnation. It is used at an industrial scale for catalyst preparation (Yang, 2003).

Takahashi et $al.$ (2000) used the incipient wetness method with activated alumina and a $CuCl_2$ solution. After the subtrate had imbibed the solution containing the salt into its pore structure, the sample was heated at 100°C to remove the solvent. Then, Cu^{2+} was reduced by temperature-programmed reduction to Cu^+.

For activated carbon, Han et $al.$ (2003) prepared the activated carbon-supported $CuCl_2$ by the conventional impregnation method. Copper Chloride solution was prepared by dissolving $CuCl_2$ in ethanol. Activated carbon particles were impregnated with copper chloride solution, followed by drying under a flow of nitrogen gas at 150°C for 3 h.

CuCl is one of the most water-insoluble salts for π-complexation. So many researchers tried to find a solvent that can dissolve CuCl. Hirai *et al.* (1985) used 1:1 (v/v) acetronitrile-water mixture. The sample was impregnated at 20°C for 4 h, and then the liquid phase was thoroughly removed at 80°C, 7 mmHg for 4 h.

Wang *et al.* (1997) used a cuprous solution by mixing cuprous chloride, ammonium hydroxide, ammonium cittate and deionized water. Ammonium citrate was used as the dispersant, which stabilizes Cu^+ and should not be decomposed. Then the impregnated sample was dried at 40°C in vacuum under the flow of nitrogen, and then heated up to 200°C under nitrogen atmosphere.

2.4 Desorption

The desorption or regeneration step is quite important in the overall process. First, desorption allows recovery of adsorbent for further cycles. In a few cases, desorption is not practical, and the adsorbate must be removed by thermal destruction or another chemical reaction, or the adsorbent is simply discarded (Rousseau, 1987).

Hernández-Maldonado *et al.* (2004) regenerated the layered adsobents by using two techniques. In regeneration of activated carbon/Cu(I)-Y zeolite by using solvents, the CCl₄, showed the highest capacity recovery when compared with DMF, methanol and toluene. When regenerated by flowing air at 350 °C for 6 hours followed by autoreduction, the CDX/Cu(I)-Y can be fully regenerated while the activated carbon/Cu(I)-Y can recover only 85%. Xue *et al.* (2005) found that the regeneration of CeY-zeolite (Na) was accomplished by calcining at 450°C in air for 2 hours. More than 90% of that of the first adsorption was recovered. They suggest that the regeneration of the adsorbent is possible by controlling the calcination conditions. Reut *et al.* (2006) investigated the desorption of thiophene and xylene from CuCl₂/SiO₂ and Na-X zeolite by using solvent, toluene, heptane, and 2% methanol in heptane. For CuCl₂/SiO₂, they observed that toluene can easily displace thiophene and xylene molecules from the active sites on this adsorbent. For other solvents, it can be seen that nearly 100% recovery of adsorption capacity was achieved. However, this was not the case with Na-X zeolite as the adsorbent for thiophene. Desorption of spent Na-X zeolite was then carried out at higher

temperature. Kaewboran (2006) investigated the desorption of NaX after desulferized the sulfur compounds such as 3-MT and BT in simulated gasoline and DBT in simulated diesel by heating technique at 400°C. She found that this method is not proper for DBT but 3-MT and BT. In addition, the recovered adsorption capacity of NaX that adsorbed with BT was a slightly lower than 3-MT. Wang *et al.* (2007) studied the desorption of $PdCl_2$/activated carbon after saturated with the model jet fuel. The desorption was conducted in a static bath of solvent at room temperature and 50 °C. The results showed that the amount of sulfur desorbed depended on the time and temperature. With increasing desorption time, the amount of sulfur desorbed reach a constant value. They also found that ultrasound was an effective technique for regenerating spent $PdCl_2$/activated carbon.