Desulfurization of FCC Gasoline: Novel Catalytic Processes with Zeolites

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Abstract

New regulations aim to achieve a drastic sulfur emission reduction in fuels and impose very low sulfur concentration caps (30 ppm in gasoline and 15 ppm in diesel) that will be in full force in 2009. FCC gasoline represents almost 40% of the total gasoline pool and it is the major sulfur contributor, with up to 85–95%. To deal with this situation, most refiners have adopted post-treating FCC gasoline processes given they are more viable and less costly for meeting sulfur environmental regulation limits. In this respect, one should notice that conventional hydro-treating of FCC gasoline removes sulfur decreasing gasoline quality with octane number losses. The use of hydrogen also adds important costs to the desulfurization. As a result, new promising catalytic desulfurization processes are being proposed using zeolites as adsorbents/catalysts. These new approaches may lead to novel technologies, for example, with the case of gasoline de-hydrosulfidation with no hydrogen addition and alternatively to adsorption processes with co-feeding of an H-donor being pioneered at CREC University of Western Ontario. In both approaches sulfur is efficiently removed leaving the gasoline octane number index intact. The zeolite structure, the framework composition and the properties of the charge compensating cations are all parameters with major impact on catalytic desulfurization. In particular, shape selectivity is expected to play an important role in determining product selectivity when condensation reactions are significant. In this respect, the H-ZSM5 zeolite appears to have the adequate balance of Brönsted acidity and Lewis basicity to efficiently convert thiophene to H_2S, with minimal transformation of benzothiophene and

oligomers into coke. From a chemical reactor engineering point of view, novel gasoline desulfurization can be implemented using both fixed and fluidized bed reactors. Fluidized circulating bed reactors display high sulfur removal ability allowing frequent catalyst removal from the catalytic bed and coke combustion in a twin fluidized regeneration unit. Fixed bed units with adsorption/desorption cycles, used in conjunction with and without H donor co-reactants, lead to selective adsorption and efficient removal of sulfur species.

1. INTRODUCTION. NEW ENVIRONMENTAL REGULATIONS

Environmental regulations regarding transportation fuel quality and emissions from refineries are currently critical issues affecting the fuel industry. The primary goal of the recently proposed regulations (by the Directive of the European Parliament and the Environmental Protection Agency (EPA) Clean Air Act (Tier 2)) is to reduce the sulfur content of transportation fuels (Babich and Moulijn, 2003 and references therein). The Tier 2 gasoline sulfur control program begun in 2004 and mandated that the average sulfur content of gasoline shipped from U.S. refineries to be lowered to 30 ppm or less between 2004 and 2008 (MathPro Inc., 2003). Canada outlined regulations involve a two-step plan demanding 150 ppm sulfur in gasoline by 2002 and 30 ppm average by 2005 (Kaufmann *et al.*, 2000). In Europe, the Auto-Oil Program I directive mandated a sulfur content of 150 ppm as of January 2000, which has to be lowered to 50 ppm or less by 2005 under the Auto-Oil Program II. In Japan, the gasoline regulations specified a maximum sulfur content of 100 ppm by 2003, with the current average sulfur content being about 35 ppm (Hagiwara, 2001).

Commercial gasoline is made up of different fractions coming from reforming, isomerization and fluid catalytic cracking (FCC) units. Those coming from the reforming and isomerization units are produced from distillation cuts, and consequently contain little or no sulfur because the sulfur-containing compounds present in crude petroleum have generally high boiling points and the feedstocks used in the isomerization and reforming units are generally hydrotreated (Brunet *et al.*, 2005). On the contrary, the atmospheric residues or the vacuum distillates which constitute FCC feedstock contain significant amounts of sulfur, 0.5–3 wt. % (Valla *et al.*, 2004). Consequently FCC gasoline, which represents 30 – 40% of the total gasoline pool, is by far the most important sulfur contributor in gasoline, up to 85–95% (Kaufmann *et al.* 2000, Babich and Moulijn 2003, Brunet *et al.* 2005). In recent years a large number of articles dealing with the sulfur distribution in FCC effluents have been published (Shorey *et al.* 1999; Yi and Xia 2001, 2002, 2004; Corma *et al.* 2001; Leflaive *et al.* 2002; Hernandez *et al.* 2003; Dupain *et al.* 2003; Valla *et al.* 2004; Salazar *et al.* 2004). The most important class of sulfur compounds present in FCC gasoline is made of thiophene and its alkyl derivatives in addition to benzothiophene (Leflaive *et al.*, 2002). Most of these compounds are not present in the FCC feedstock and they could either both result from the direct transformation of the sulfur compounds present in the feedstock or result from the recombination of FCC products (Leflaive *et al.*, 2002).

The new regulations make it necessary to remove these sulfur organic compounds from the FCC gasoline almost completely and a great deal of research has also been devoted recently to this important issue. Conventional hydrotreating

of FCC gasoline decreases its quality by octane number loss. Moreover, the use of hydrogen adds important costs, and this explains why the latest gasoline desulfurization studies are orientated to desulfurization processes free of hydrogen. There are some theoretical and experimental studies that support the use of zeolites as adsorbent and cracking catalyst of sulfur compounds. This chapter reports a detailed discussion of new gasoline desulfurization processes that use zeolites as catalyst in both fixed and fluidized bed reactors. The reaction mechanisms and the kinetics modeling of theses systems are also reviewed. In the same line of thinking the present chapter considers the new reactor engineering approach needed for the successful application of this technology.

2. SULFUR COMPONENTS IN FCC GASOLINE

The main sulfur components of FCC gasoline are light mercaptans and disulfides (20 wt %), thiophene or alkyl-thiophenes (50 wt %) and benzo-thiophene (30 wt %) (Valla *et al.*, 2004). Alkylthiophenes, which are typically in the boiling range of gasoline, include three and four carbon atoms-substituted thiophenes (C3- and C4-thiophenes) being difficult to establish whether these are poly-methylated or longer chain-substituted thiophenes.

Table 1. Gas chromatographic analysis of thiophene derivatives in FCC naphtha (Yin and Xia, 2004)

Peak no	Compounds	Percent ratio of total Thiophenes (sulfur %)	Sulfur content (ppm)
3	Thiophene	6.3	69.2
4	2-Methylthiophene	10.0	109.8
5	3-Methylthiophene	13.8	152.6
8-12	Dimethylthiophenes	35.4	389.8
13	Unknown thiophene	4.0	43.9
14	Isopropylthiophene	2.4	26.4
15	Methylethylthiophene	4.2	46.1
16	Trimethylthiophene	5.6	61.5
17	Unknown thiophene	1.6	17.6
18	Trimethylthiophene	4.1	45.0
19-24	4-Carbons-alkylthiophene	10.5	116.4
25	Unknown thiophene	2.1	23.0

Data reported by Yin and Xia (2001, 2002, 2004) confirms that thiophene sulfur represents a large fraction of the total sulfur content in FCC gasoline (60 wt% and over). By using gas chromatography these authors detected more than 20

different kinds of thiophenes among which a certain number could be identified by GC/MS analysis (Table 1).

2.1. Origin of sulfur components in FCC gasoline

A semi-quantitative distribution of sulfur species in various feedstocks is reported in Table 2.

Table 2. Distribution of sulfur impurities in three different FCC feedstocks A, B and C (Brunet *et al.*, 2005)

	Feed A	Feed B	Feed C
Mercaptans and sulfides	7	12	26
Thiophenes	59	56	42
Benzo and multiring thiophenes	30	17	29
Oxidic sulfur	4	15	3

Additionally to sulfur species present in FCC feedstocks, sulfur impurities falling in the boiling range of FCC gasoline can be formed during the FCC process. Leflaive *et al.* (2002) proposed that these impurities could be produced as a result of the cracking of long alkyl chain thiophenes contained in the FCC feedstock (Figure 1 Scheme a). Alternatively, the addition of H_2S to olefins or diolefins, followed by cyclization into tetrahydrothiophenic compounds, can lead, following dehydrogenation, to thiophenic compounds (Figure 1 Scheme b). A similar conclusion was reached by Hernandez *et al.* (2003), who suggested that mercaptans could be responsible for the formation of thiophenic species in gasoline.

However, and to have a more adequate description of sulfur species genesis under FCC conditions, a number of other reactions must be taken into consideration. For instance, Corma *et al.* (2001) proposed a set of interconnected reactions for the transformation of sulfur containing compounds on FCC catalysts (Figure 2) with a role being assigned to the long chain alkylbenzothiophenes present in the feed. These species can easily be transformed, either through dealkylation or cracking of the side chain, to benzothiophene and short chain alkylbenzothiophenes, ending in the gasoline range fraction. These compounds can also undergo alkylation into heavier compounds and eventually form coke. Even more, if long chain alkylthiophenes are present in the feed, they can be transformed both into benzothiophene derivatives through cyclization and dehydrogenation and into thiophene and short chain alkylthiophenes through dealkylation or cracking of the side chain.
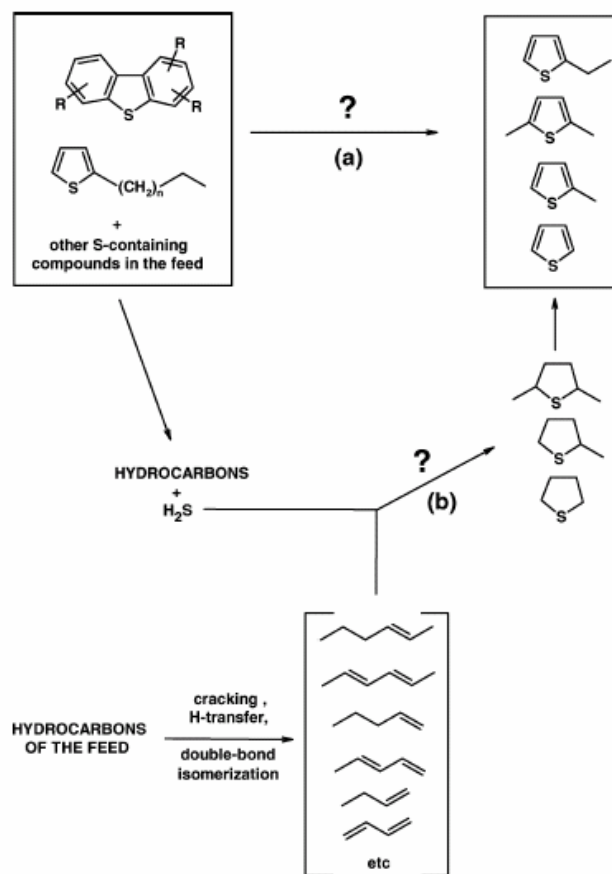
Figure 1. Possible pathways for the formation of sulfur-containing compounds present in FCC gasoline: transformation of heavy sulfur compounds contained in the feed (a); reaction of H_2S (produced by desulfurization of sulfur impurities of the feed) with olefins or diolefins resulting from the catalytic cracking of the hydrocarbons of the feed (b); cyclization of long chain alkylthiophenes formed during the process (c). (Reproduced from Applied Catalysis A: General, vol. 227, Leflaive *et al.*, "On the origin of sulfur impurities in fluid catalytic cracking gasoline-Reactivity of thiophene derivatives and of their possible precursors under FCC conditions", p. 201-215, Copyright 2002, with permission from Elsevier)

Valla *et al.* (2004, 2006) studied the cracking behavior of sulfur compounds during the fluid catalytic cracking (FCC) process. Their results indicate that thiophene is a quite stable molecule that produces, following cracking, mainly H_2S and S containing polyaromatics hydrocarbons (coke). Short chain alkyl-thiophenes can also undergo dealkylation and isomerization reactions, with

pronounced hydrogen transfer leading to H_2S and coke. Furthermore, the reactivity of alkyl-thiophenes depends strongly on the degree of their alkylation, therefore the longer the alkyl chain, the higher becomes the observed conversion. In the case of long-chain alkyl-thiophenes, the cyclization/dehydrogenation reactions producing benzothiophenes and alkyl-benzothiophenes may be significant. It was found in this respect that benzothiophene is more reactive than thiophene because it participates in alkylation reactions resulting in heavier sulfur compounds with a boiling point outside the gasoline range.
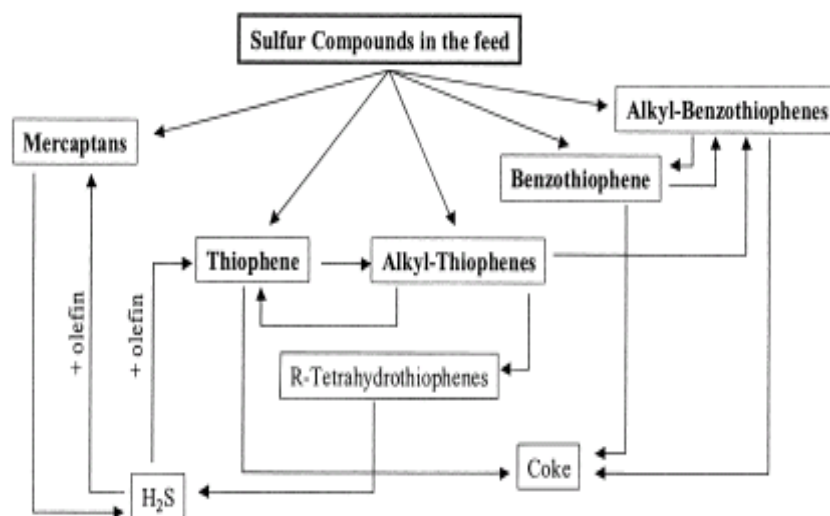

Figure 2. Interconnected reaction scheme for the formation of sulfur impurities under FCC conditions (Reproduced from Applied Catalysis A: General, vol. 208, Corma *et al.*, "On the mechanism of sulfur removal during catalytic cracking", p. 135-152, Copyright 2001, with permission from Elsevier)

Given the results described above, most sulfur compounds present in FCC gasoline range are formed during the catalytic process from the compounds containing species present in the feed. As well, reaction conditions such as temperature, feedstock partial pressure and contact time determine the relative contributions of the many reaction pathways, influencing the type and concentration of sulfur containing species (Brunet *et al.*, 2005).

3. STRATEGIES TO REDUCE FCC GASOLINE SULFUR CONTENT. PROCESSES AND ALTERNATIVES

There are three main options to be considered for producing gasoline with very low sulfur: hydroprocessing of the FCC feedstock, reduction of the sulfur content

during the FCC process and desulfurization of FCC gasoline. Each of these options has specific advantages, disadvantages and extent of development.

3.1. Hydroprocessing of the FCC feedstock

As a result of the changing refining needs, modern FCC feed pretreating units are being designed to desulfurize feedstocks very effectively. Available options for hydrotreating FCC feedstocks are conventional hydrotreating, conventional hydrocracking and mild hydrocracking. The conventional hydrotreating processes include developments made by companies such as Exxon, Shell, UOP, IFP and Haldor Topsoe. Additionally, there are recent studies developed with biocatalysts by Energy BioSystems Corporation and Petrolite Corporation, which demonstrate the value of oil enzymatic desulfurization (Hydrocarbon Publishing Company, 1997).

Among hydrocracking technologies relevant ones are the MAK Hydrocracking process of M.W. Kellogg, the Unicracking™ of UOP and the T-STAR process developed by IFP and licenced by Texaco Development Corporation (Hydrocarbon Publishing Company, 1997).

The effect of hydrotreating on the FCC feedstock and product quality was extensively studied (Shorey *et al.* 1999, Wisdom 1999, Lappas *et al.* 1999, Salazar *et al.* 2004, Valla *et al.* 2004,). It was reported that the hydroprocessing of FCC feedstock not only reduces sulfur content but also reduces nitrogen, metals, olefins, asphaltenes and poliaromatics. Polynuclear species hydrotreating, hydrogenation and cracking, lead to naphthas with higher fractions of light cycle oil (LCO) and heavy cycle oil (HCO) and reduced coke yields. Moreover, the considerable reduction of nitrogen, nickel and vanadium helps moderating catalyst deactivation providing better overall conversion. Hydrotreating also leads to alkenes and dialkenes partially hydrogenated minimizing coke and polymer gums formation. Finally, there is also a reduction in sulfur content of all FCC products, including SO_x and NO_x emissions from the regenerator.

In spite of all the claimed benefits, the hydroprocessing of FCC feedstocks requires both important investment and involves high operating costs due to the needed process severity and H_2 consumption. This explain why many refiners have adopted the post-treating FCC gasoline approach as the more viable and less costly path for meeting sulfur environmental regulations.

3.2. Sulfur gasoline reduction during FCC process

The sulfur content of FCC gasoline can be reduced during FCC process using three possible approaches: a) removing the heaviest gasoline cut, b) using new catalysts and additives and c) changing FCC operation conditions.

Figure 3 reports how sulfur, olefins and aromatics in the FCC naphtha distribute throughout the boiling range of the FCC gasoline (Shorey *et al.*, 1999). For instance, adjusting the fractionator conditions so that the heaviest 20% of the FCC naphtha is included in the LCO, it reduces the gasoline endpoint and can as a result diminish its sulfur content by as much as 60%. The drawbacks to this approach are a lower gasoline yield, higher LCO yield and no change in the sulfur content of the other products.
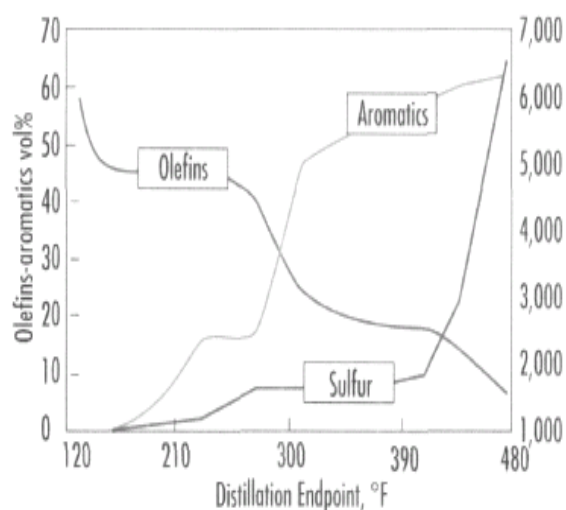

Figure 3. FCC naphtha composition (Shorey *et al.*, 1999).

FCC catalyst properties such as zeolite unit cell size, matrix activity and alumina content can be adjusted to provide a reduction of sulfur species contained in gasoline of about 10%. Nevertheless, the higher hydrogen transfer that result of those adjustments can introduce non-desirable selectivity changes such as lower LPG olefinicity and higher coke and dry gas yield (Harding *et al.* 2001, Lappas *et al.* 2004).

FCC additives can also be used for the reduction of sulfur in gasoline. For instance, commercial additives such as GSR-1, SuRCA (with GSR-4 technology) and GFS-2000 are claimed to provide commercial gasoline sulfur reductions in the 15–35% range (Hernandez *et al.* 2003, Harding *et al.* 2001). Andersson *et al.* (1999) produced additives for sulfur-compound cracking by depositing various metals (Zn, Mn, Zr, Co) and metal oxides on different supports (alumina, titania, and hydrotalcite) using a micro-emulsion technique. These authors claim to attain 80% sulfur reduction in gasoline, this being accomplished with a significant loss in gasoline as well as an increase in both gases and coke yield. More recently, Vargas *et al.* (2005) demonstrated that zinc aluminate may potentially be a valuable additive for gasoline sulfur reduction. On the basis of these results, these

authors claimed that the Lewis acid (LA) sites are the main responsibles for the adsorption of sulfur containing species such as thiophene. It is however the presence of Zn that renders these sites active enough to perform sulfur removal. Even though these catalytic technologies will probably be improved significantly over the next few years, it appears they are not be able to provide the high extent sulfur reductions required by the new legislation very soon.

Finally, the adjustment of FCC operational conditions, such as the reactor temperature and mass catalyst/oil ratio (CTO), can also affect the sulfur content in gasoline. For instance, a reduction of 5.5 K in the FCC temperature decreases 7% the sulfur content with an octane loss of 1.5 units. This approach is in clear contrast with the worldwide tendency in most refineries of increasing the temperature in the FCC riser cracker to maximize the overall conversion, producing higher levels of light olefins and octane enhancer species (Hydrocarbon Publishing Company, 1997). More recently, Dupain *et al.* (2003) studied the cracking behavior of organic sulfur species under realistic FCC conditions varying the process parameters (CTO between 2 and 8 g cat/g oil, residence time between 1.2 and 5 s, temperatures of 798, 828 and 858 K). It was found that under typical FCC conditions the residence time and CTO ratio are possible too low to enable high hydrogen transfer rates. Consequently, stable sulfur species, such as thiophenes, benzothiophenes and dibenzothiophenes are unlikely to be catalytically cracked.

Thus, a review of the literature shows that it appears rather difficult to envision that gasoline and diesel sulfur specifications could be met by varying the FCC process parameters (temperature, CTO ratio and residence time) so that other more fundamental based approaches are required.

3.3. FCC gasoline desulfurization

The third possible approach to achieve low sulfur FCC gasoline is through post-treatment FCC processes. The hydrodesulfurization of FCC gasoline requires less severe operation conditions and less H_2 consumption than the hydrotreatment of FCC feedstock, thus the post-treatment demands the minimum investment and is the less costly route for meeting the Tier 2 gasoline sulfur standards. This economic advantage has promoted the development of new naphtha desulfurization processes and technologies with several recent review articles published in this topic (Babich and Moulijn 2003, MathPro Inc. 2003, Kaufmann *et al.* 2000, Hagiwara 2001, Brunet *et al.* 2005, Song 2003, Plantenga and Leliveld 2003).

In 1997, the only commercial technology for controlling the sulfur content of full-range FCC naphtha was what nowadays is called "conventional hydrotreating". A number of technology's providers that offered conventional

hydrotreating processes accumulated considerable commercial experience. They were reliable and well-understood processes, and could accomplish the necessary degree of sulfur contain species removal and as a result sulfur content control in gasoline. However, conventional FCC naphtha hydrotreating processes are expensive because they are non-selective. In the course of removing the sulfur, many of the olefins species contained in the FCC naphtha are saturated. Olefin saturation leads to octane loss (> 10 numbers) and hydrogen consumption, which accounts for the high cost of conventional hydrotreating. The average cost of achieving the Tier 2 gasoline sulfur standard with conventional hydrotreating is estimated in the range of 5¢/gal of complying gasoline (assuming that FCC naphtha constituted 30–40 vol% of the gasoline pool) (MathPro Inc., 2003).

New technologies for FCC naphtha desulfurization fall into three categories: a) *Selective hydrotreating*. The SCAN fining, PrimeG+, CDHydro, CDHDS and OATS processes are in this category. These processes achieve desulfurization with little olefins saturation and an octane number loss of between 1 to 2 points.
b) *Non selective hydrotreating + octane recovery*. This includes the OCTGAIN and ISAL processes, which reach desulfurization with partial or total olefins saturation, and recover most of the lost octane via isomerization of saturated hydrocarbons.
c) *Sorption technology*. One can consider in this category the S Zorb process in fluidized beds for hydrogenation adsorption, the TREND process in moving bed (under development, not yet publicly unveiled), and the IRVAD process in slurry to move the adsorbent (development apparently abandoned). Desulfurization takes place under the presence of hydrogen in order to accelerate the reaction between the sulfur compounds and the adsorbing agent.

Table 3. Refiners' Choices of Processes for Full-Range FCC Naphtha Desulfurization, as of March 2003 (MathPro Inc., 2003)

Process	Technology	Process Licensor	Number of Refineries
SCANfining	Selective HDS	Exxon Mobil	26
CD Hydro /CD HDS	Selective HDS	CD TECH	≈ 30
ISAL	HDS + Octane Recovery	UOP	≈ 5
S Zorb G	Sorption	Phillips	≈ 10
Prime G+	Selective HDS	IFP	> 60

Notes:
1. All process names are trademarked
2. HDS denotes Hydrodesulfurization
3. The number of refineries includes both US and foreign refineries.

Table 3 summarizes the various technologies and the number of units already installed or in the process to being installed to comply with the Tier 2 gasoline sulfur standard (MathPro Inc., 2003). These naphtha desulfurization technologies decrease the FCC gasoline quality given olefins, main contributors to the gasoline octane number, are hydrogenated into paraffins. Additionally, during hydrodesulfurization the sulfur removed in the form of hydrogen sulfide (H_2S) may react with the olefins forming sulfur containing molecules such as mercaptans. As well post-treatment desulfurization processes are rather expensive given they involve the use of costly hydrogen. Taking these aspects into consideration, a hydrogen-free desulfurization process could present major cost savings over HDS. In this sense, there are new desulfurization processes that support the use of zeolites as selective sulfur adsorbent and cracking catalysts. A detailed description of these processes will be given in upcoming sections.

4. ZEOLITES AS A SULFUR ADSORBENT AND A CRACKING CATALYST

First results about selective adsorption of thiophene in benzene mixtures using ZSM-5 zeolites, either in the gaseous or in the liquid phase, were reported by Weitkamp *et al.* (1991). Most of the adsorption experiments were conducted in a flow-type apparatus with a fixed bed adsorber. Experiments were developed using a multi-component saturator with a carrier gas (nitrogen) saturated with vapors of benzene (pBz = 23.3 kPa) and thiophene (pTh = 0.18 kPa). The adsorber effluent was analyzed periodically (typically every 4 min) via on-line capillary gas chromatography and breakthrough curves for benzene and thiophene were simultaneously obtained. To explore whether thiophene can be removed in the liquid phase as well, either a mixture of 0.5 wt.% thiophene and 99.5 wt.% benzene or a real coke-oven benzene was pumped through a column filled with adsorbent. Desorption experiments were performed by flushing the adsorbent with nitrogen while slowly increasing the temperature from 323 to 623 K within two to three hours and keeping the final temperature for an additional three hours. The desorbing components were collected in a cold trap and analyzed by gas chromatography. Weitkamp *et al.* (1991) also investigated the potential of a variety of other zeolites with different pore widths and pore geometries. It was only with zeolite ZSM-11, which is structurally related whit ZSM-5 (both belong to the pentasil family) that comparable adsorption selectivities were observed. Thus these authors concluded that structural features of the zeolite channel system must play an important role in thiophene/benzene separation. King *et al.* (2000) used H-ZSM5 to adsorb thiophene, methyl-thiophene and dimethyl-thiophene from their gaseous mixtures with toluene or *p*-xylene, and found that organosulfur molecules were selectively adsorbed relative to the more abundant arenes. One

should notice that adsorption capacities were slightly lower (0.13 thiophene/Al at 363 K and 0.1 kPa of thiophene) than those reported by Weitkamp *et al.* (1991), possibly because of the higher temperatures, lower thiophene pressures and competitive adsorption with larger arenes.

Garcia and Lercher (1992, 1993) studied the adsorption and reaction of H_2S, ethanethiol and thiophene on ZSM-5 zeolites. The adsorptive capacity of the zeolite was investigated by means of transmission - absorption IR spectroscopy. Self-supporting disks of zeolite samples (8-10 mg/cm^2) were pressed and placed in a sample holder at the center of a small furnace in the IR beam. The IR cell was evacuated to pressures below 10^{-6} mbar. For activation, the sample was heated to 873 K. The sorption experiments were carried out *in situ* at room temperature and varying partial pressures. After evacuation at room temperature, temperature-programmed desorption (TPD) was made *in situ* with a temperature increment of 10 K/min up to 873 K. The gas phase was analyzed with a quadrupole mass spectrometer directly connected to the vacuum system.
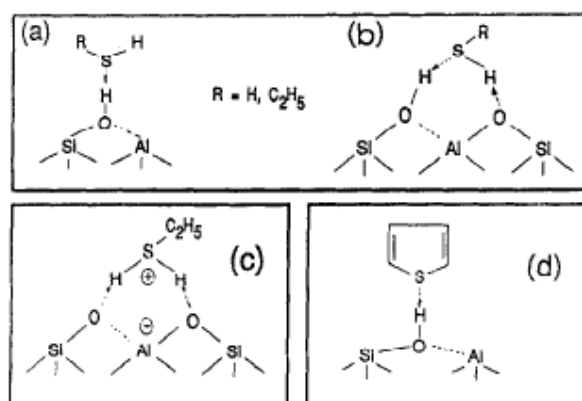

Figure 4. Models proposed for the hydrogen bonding of the sulfur containing molecules with the SiOHAl sites of H-ZSMS: (a) linear structure (b) cyclic structure; (c) protonated cyclic structure (only found with ethanethiol); (d) hydrogen bonding of thiophene (Reproduced from Journal of Molecular Structure, vol. 293, Garcia and Lercher, "Hydrogen bonding of sulfur containing compounds adsorbed on zeolite H-ZSM5", p. 235-238, Copyright 1993, with permission from Elsevier).

On the basis of their results, Garcia and Lercher (1992, 1993) confirmed that at room temperature H_2S and ethanethiol adsorb molecularly on H-ZSM5 through hydrogen bonding the sulfur atom to the SiOHAl groups of the Zeolite. They concluded that the adsorbed H_2S and ethanethiol molecules assumed different adsorption structures at the strong Brønsted acid sites: (i) an hydrogen

bonded linear form, where the sulfur acts as electron pair donor to the proton of the SiOHAl site (Figure 4.a), (ii) an hydrogen bonded cyclic form, the sulfur atom acts as electron pair donor to the proton of the SiOHAl acid site, and one of the hydrogen atoms of the H_2S or ethanethiol interacts with the neighboring oxygen atom of the zeolite framework (Figure 4.b) and (iii) a protonated ethanethiol molecule hydrogen-bonded to the surface oxygens (Figure 4c).

In the case of thiophene, they conclude that initially the thiophene hydrogen bonds to the SiOHAl groups (Figure 4). This interaction is followed by ring opening with the adsorbed intermediate tentatively described as olefin-thiol-like species, and oligomerization reactions promoted by the strong acidity of the H-ZSMS zeolite. Moreover, a number of parallel and consecutive reactions including cracking, cyclization, alkylation, and condensation yield a variety of alkylated aromatics and condensed rings, precursors for coke deposition in the pores and at the external surface. A tentative reaction scheme for the surface reactions of thiophene on H.ZSM5 is designed by Garcia and Lercher (1992, 1993) (see Figure 5).
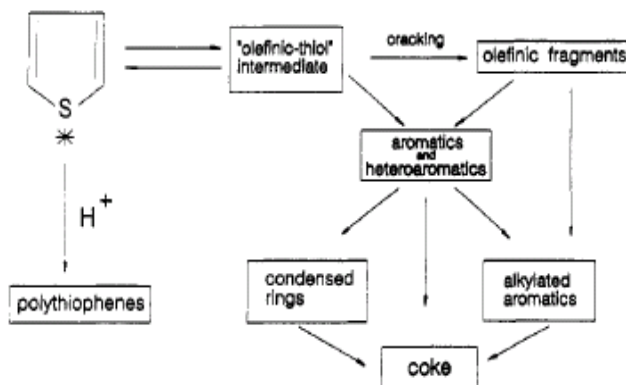

Figure 5. Reaction scheme for the surface reaction of thiophene on H-ZSM5 (Reprinted with permission from J. Phys. Chem., vol. 96, Garcia C. and Lercher J., "Adsorption and surface reactions of thiophene on ZSM5 zeolites", p. 2669-2675, Copyright 1992 American Chemical Society)

Soscun *et al.* (2002, 2004), reported theoretical studies on the structural, vibrational, and topologic properties of the charge distribution of the molecular complexes between methanethiol CH_3SH, thiophene and a series of Brønsted acid sites of zeolites, modeled as the $(SiH_2)_9(O)_9Al(OH)_2$, $H_3SiOHAlH_3$, $(OH)_3Si(OH)Al(OH)_3$ and $H_3Si (OH) Al (OH)_2 O SiH_3$ clusters. These authors found that the sulfur–zeolite molecular complexes are energetic and structurally stable, and that the hydrogen bonding between the S atom of thiophene or CH_3SH

and the OH bridge of zeolite clusters (S—HO) is very weak. The analysis of the topologic properties of the complexes and the isolated molecules indicated that additional chemical interactions occurred between the O atoms of the zeolite network and the H atoms of the CH_3SH, increasing the stability of the complexes. These results are in agreement with experimental observations of the sulfur–zeolite formation van der Waals complexes, described by Garcia and Lercher (1993) (see Figure 4).

5. THE ZEOLITE STRUCTURE AND ITS INFLUENCE IN THE SULFUR SPECIES CRACKING

The zeolite structure, the framework composition and the properties of the charge compensating cations are all parameters that can be expected to have significant impact on the desulfurization catalytic activity and selectivity. In particular, shape selectivity it is expected to play a role in determining product selectivity when condensation reactions are important. A discussion of zeolite structure influence in sulphur species conversion is detailed in the following sections.

5.1. Y and USY zeolites

Zeolite Y is the synthetic form of Faujasite, and has a Si/Al ratio between 2 and 5. Its three dimensional framework has two main cages: the large supercage results from an assembly of the basic units, the sodalite cages. The spherical supercages are approximately 13 Å diameter. Access to the supercages is afforded by four 12-membered ring windows about 7.4 Å in diameter, which are tetrahedrally distributed around the center of the supercages. Cations can occupy three positions in Y zeolites: the first type is located on the hexagonal prism faces between the sodalite units, the second type is located in the open hexagonal faces and the third type is located on the walls of the supercage (Tonetto *et al.*, 2004).

Thiophene cracking on USY at 763 K in N_2 shows products such as propane, propylene, isobutane, butenes and sulfur compounds, including H_2S, methyl-thiophenes and benzo-thiophene. Significant coke deposits on the USY zeolite, which illustrates that dehydrogenation of hydrocarbons or hydrocarbon fragments or sulfides take place during the reaction.

On the other hand, thiophene in n-heptane (sulfur content 0.33 % or 3300 ppm) displays a reduction of 61% sulfur at 763 K. The maximum thiophene conversion is found at 673 K with the same trend being observed for H-ZSM5. Benzothiophene conversion remains unaffected with temperature, which suggests that benzothiophene formation is directly related with thiophene cracking. The USY zeolite however, cannot crack selectively thiophene to form sulfides.

Comparing thiophene and alkyl thiophene in gasoline is appears to be easier to desulfurize alkyl thiophene via cracking over specially prepared catalysts with the USY zeolite as the active component. The conversion sequence in these cases is as follows: thiophene < 2 or 3 methylthiophene < C2 substituted thiophene < C3 substituted thiophene< C4 substituted thiophene (except benzothiophene).

In gasoline distillates there are many thiophene species with different degrees of alkyl substitution (near 88%). Being thiophene a Lewis base, it will likely adsorb on Lewis acidic sites. Thus, a Brönsted acidic site is considered not to be the best site for adsorption, even if there is the possibility of H-bonding, as predicted with cluster approximations. As a result, more detailed site models are required to reproduce the actual site in the zeolite structure.

5.2. Mordenite

Large pore mordenite (MOR) is a one-dimensional zeolite consisting of main channels parallel to the crystal plane. The channels have an elliptical cross section of a 12 member ring with a diameter of 7x 6.5 Å. Single crystal refinement of dehydrated Na-MOR has revealed five different sites for cation location. The number of the cations depends on Si/Al ratio. For MOR with Si/Al ratio of 10, each unit cell contains three Na cations located in side channel and two Na cations located in the intersection between eight ring and main channel.

Studies with mordenites, given its micropore size are important to understand the role of geometry in thiophene and derivatives cracking and how the zeolite structure affects the transition complex of thiophene derivatives (from benzothiophene and others), especially changing the alkoxide character to carbocationic character. Thiophene forms trimers and larger oligomers on cation exchanged Y zeolite, mordenite, and montmorillonite.

Thus, given the relatively large size of the channels in Mordenite allowing both oligomerization and polymerization, these materials are certainly not recommended for gasoline desulfurization with respect to others, case of ZSM5 zeolites, with hindered diffusion in small pores preventing the above mentioned reactions.

5.3. BETA and ZSM5 zeolites

Chica *et al.* (2004) studied the adsorption and reaction of thiophene on MFI (5.1 x 5.5 Å), BETA (6.6 x 6.7 Å) and FAU (7.4 x 7.4 Å) zeolites with similar Si/Al molar ratio (Si/Al = 13). These authors also studied the effect of Al content in FAU structures (Si/Al molar ratio 6, 13, 33 and 85). Thiophene uptakes were 1.7, 2.2 and 2.9 thiophene /Al on H-ZSM5, H-BETA and HY at 363 K and 1 kPa thiophene. This indicates that the adsorption depends on channel size and zeolite

structure. Uptakes were much lower than those required to fill zeolite channels with condensed thiophene, which were estimated to be 2.8, 4.1 and 7.0 for the same zeolites respectively. The adsorption isotherms also demonstrated that the binding energies and stoichiometry of thiophene depend on zeolite structure.

Chica et al (2004) observed that thiophene oligomers are indeed formed on Brönsted acid sites during adsorption at 363 K. The dynamics of desorption was measured for HY, H-ZSM5 and H-BETA. ZSM5 showed two desorption peaks for thiophene (534 and 668 K), whereas the other two showed only one at 525 K. The amount of thiophene desorbed and unreacted per Al was the highest for HY and the lowest on H-ZSM5. At the same time, the amount of H_2S desorbed increased with Al content for all zeolites. Benzene, toluene, benzothiophene and ethene formed in smaller amounts in BETA and Y than on ZSM5. Larger amounts of methylthiophene and propylene were found when BETA and Y were used. These findings can be related to the size effect on transition states. Bulky transition states appear to be favoured within larger channels in Y and BETA. Smaller ZSM5 channels would enhance the interactions of butylthiophene species with acid sites or adsorbed thiophene derived species forming desorbable molecules. As well, studies on competitive adsorption with toluene demonstrated high selectivity in the case of H-ZSM5.

Acidity in BETA zeolites has been measured with different tools. In a recent manuscript Jung *et al.* (2004) reported acidity as measured via TPD with ammonia. These authors concluded that MOR with Si/Al ratio of 10 and MFI with 25 were the most acidic in terms of acid strength and number of acid sites. BETA (Si/Al=13) and FAU (Si/Al=2.65) had a small number of strong acid sites. On this base, Jung *et al.* (2004) concluded that the number of strong acid sites does influence activity, but not selectivity, and that the pore-shaped sinusoidal path in the MFI-ZSM5- suppressed the formation of large hydrocarbons.

Looking at the order of Brönsted acidity, a HY = H-BETA < H-ZSM5 order was assigned. While considering the topological density however, a FAU (Y) < BETA < MFI order was considered. Based on n-octane reaction coupled with ammonia TPD (Jung *et al.*, 2004), it appears acidity follows the trend as represented with topological density. It can be thus, concluded that the O character in the case of H-ZSM5 is basic and non neutral, with basicity following the MOR>MFI>CHA>FAU order as postulated by Brandle and Sauer (1998) using cation exchanged zeolites.

5.4 ZSM5 doped with group I and group II metals

The role of Lewis centers on thiophene and other sulfur-containing species desulfurization is a topic of key importance. This subject has been addressed considering thiophene desulfurization on Na-ZSM5 as a reference.

Thiophene oligomerization occurs on acid solids with the reaction being essentially arrested after 0.3 h. This is the result that both in H-ZSM5 and Co/H-ZSM5 acid zeolites the transport in the zeolite channels becomes restricted via formation of coke. On the other hand, in Na-ZSM5, thiophene oligomers are not formed due to the absence of acid sites. Thiophene is adsorbed via potential interactions with Na cations. One should notice that similar amounts of thiophene are retained in both H-ZSM5 and Na-ZSM5, even when the zeolite sample does not contain Brönsted acidic OH groups.

Under helium atmosphere, the amount of thiophene adsorbed on Na-ZSM5 is higher than the amount adsorbed on H-ZSM5 at 303 K. Even more, the thiophene removed with He/Na-ZSM5 is similar to that separated with H_2/H-ZSM5.

Regarding desorption in Na-ZSM5, unreacted thiophene desorbs in the form of two peaks: a low temperature peak and a high temperature peak. The high temperature peak shows a much larger fraction of desorbed thiophene from Na-ZSM5 than on H-ZSM5 or Co/H-ZSM5.

Cations can as well increase the rate of thiophene desulfurization using propane as a co-reactant. The desulfurization of thiophene occurs in this case via the hydrogen transfer from alkanes on cation-modified H-ZSM5 zeolites, with desulfurization becoming faster when Zn^{+2} or Co^{+2} are present in the zeolite structure.

Finally, alkane dehydrogenation can also be coupled with thiophene hydrogenation on surfaces to increase thiophene desulfurization and propane dehydrogenation simultaneously.

When comparing IR studies of thiophene on H-ZSM5 and on Na-ZSM5, one can notice that on the H-ZSM5 the characteristic IR band of 3610 cm^{-1}, related to hydrogen bonding interactions of thiophene with the acidic OH groups, shift towards a broader 3200 cm^{-1} band. For longer contact times, the intensity of the 3610 cm^{-1} band decreases while the 2900, 2350 and 1410 cm^{-1} bands gaining importance. As well, new IR absorption lines develop at 3120, 3080 and 1250 cm^{-1}, with these bands being attributed to a condensed thiophene phase within zeolite channels. The bands at 2900 cm^{-1} , 2350 cm^{-1} are assigned to a CH_2 bonded to a C=C or to CH_2 bonded to S and to S-H groups with OH respectively. These changes show that thiophene molecules attached near OH groups react at 303 K forming products that remain adsorbed on the surface. Ring opening and polymerization appear to be initially favoured by high temperatures but the products formed either desorb or dehydrogenate further into active organosulfur surface species with lower IR cross sections.

On Na-ZSM5, 3150 and 3100 cm^{-1} bands are observed which indicate that a condensed thiophene phase develops. This is consistent with Na-ZSM5 only having weak Lewis acidic sites and no Brönsted sites making the Na-ZSM5

zeolite inactive as a catalyst. As a result, no ring opening or oligomerization reactions of thiophene derived species are observed and one can thus, conclude that the Na-ZSM5 is inactive to gasoline desulfurization.

On the other hand in H-ZSM5, there is abundance of Brönsted acidic and Lewis basic sites (O^{-2}) with both being critical for ring opening. This combination of Lewis basic/Brönsted acidic sites is particularly valuable when an external source of hydrogen is provided; such is the case of long hydrocarbons being present.

Xu *et al.* (2006) studied the effect of Ca^{+2} substitutions in the electrostatic field of zeolites. Oxygen and propane adsorption at room temperature demonstrate that the electrostatic field of Ca^{+2} increases in the order Ca-Y<Ca-MOR<Ca-ZSM5. Results show that the geometrical structure of the zeolite determines to a large extent both activity and selectivite partial oxidation of propane on Ca^{+2} exchanged zeolites. The partial oxidation intermediate involves the formation of an ion-pair of hydrocarbon and oxygen. Basicity of the lattice O is thus, critical. One should notice that on ZSM5 zeolites a very broad band with maximum intensity around 3470 cm^{-1} belongs to perturbed OH groups interacting with the zeolite lattice oxygen. FTIR of ZSM5 reported by Yu *et al.* (2003) demonstrates that in the dehydrated form a broad band of lower intensity develops in this zone indeed. Thus, it appears that electrostatic fields in Ca-ZSM5 are much higher than in MOR or Y and, they may provide an optimal ratio between Brönsted acid sites, Ca^{+2} cations (and Lewis basic sites derived from the substitution) enhancing reaction activity.

6. MECHANISTIC APPROACHES DESCRIBING SULFUR SPECIES CONVERSION OVER ZEOLITES

Several studies show that sulfur species conversion on zeolites can not be explained on the basis of the generally accepted mechanisms involved in the HDS of sulfur species on sulfide catalysts. This section shows a review of the sulfur species conversion mechanisms over zeolites suggested in the literature.

In this respect, Welters *et al.* (1994) found that pure acidic supports had a substantial activity in thiophene desulfurization, and that the activity increased linearly with the increasing acidity strength of the materials. Thiophene HDS activity measurements were carried out in a micro flow reactor under standard conditions (673 K, 1 bar pressure, 4.0 vol% thiophene in hydrogen, and 50 STD cm^3/min). These authors suggested a direct desulfurization mechanism involving H^+ and leading to butadiyne (which was supposed to polymerize) plus H_2S through β-elimination.

This interpretation was supported by Saintigny *et al.* (1999), who in their study using density functional theory (DFT) calculations, considered two possible

mechanisms to account for the desulfurization of thiophene on acid catalysts. The first mechanism (Figure 6) does not involve hydrogen. Each of the two C–S bond cleavages in adsorbed thiophene, leading to desulfurization occurring in two steps. The first step consists of a displacement of the sulfur by a nucleophilic surface oxygen atom; the second step is a β-elimination process where another surface oxygen anion leads to the formation of a triple bond. This process repeated twice yielding butadiyne and H_2S, as proposed earlier by Welters *et al.* (1994).
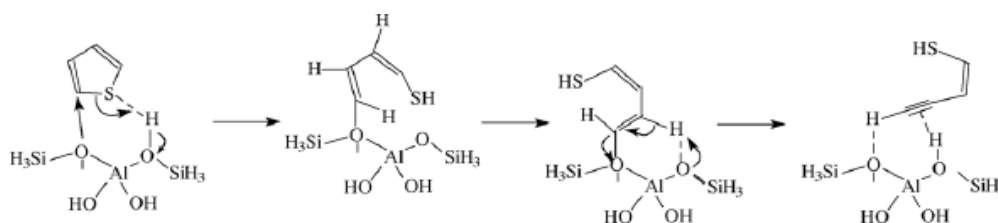
Figure 6. Mechanism of C–S bond cleavage in thiophene and desorption of the intermediate enethiol over a pure acidic zeolite in the absence of hydrogen (Reproduced from Applied Catalysis A: General, vol. 278, Brunet *et al.*, "On the hydrodesulfurization of FCC gasoline: a review", p. 143-172, Copyright 2005, with permission from Elsevier).
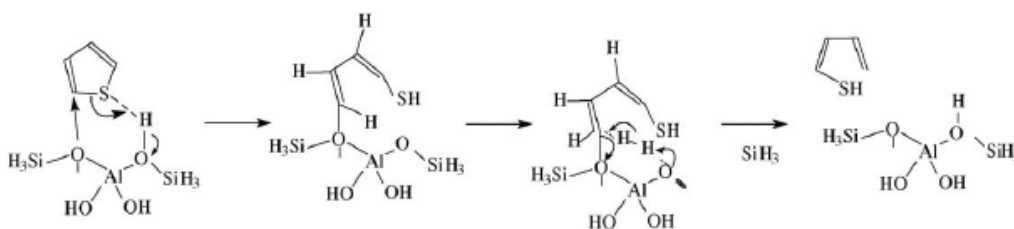

Figure 7. Mechanism of C–S bond cleavage in thiophene and desorption of the intermediate enethiol over a pure acidic zeolite in the presence of hydrogen (Reproduced from Applied Catalysis A: General, vol. 278, Brunet *et al.*, "On the hydrodesulfurization of FCC gasoline: a review", p. 143-172, Copyright 2005, with permission from Elsevier).

The second mechanism considered by Saintigny *et al.* (1999) is a reaction sequence with pre-hydrogenation. According to this, both C–S bonds in thiophene are broken through a process involving two consecutive nucleophilic displacement reactions. The first step is a chemical event shared with the previous mechanism (Figure 6) and leads to a vinylic enethiol adsorbed at a surface oxygen atom. The second step involves the displacement of the oxygen by a hydride ion

provided by dihydrogen adsorbed on adjacent oxygen with a basic character (Figure 7). This process repeated twice leading as a result to desorption of butadiene and H_2S.

Shan *et al.* (2002) investigated the cracking of thiophene and alkyl-thiophene species on USY zeolite at 763 K, using online pulse-reaction chromatography, MS transient response technique, and fixed bed reactor. Their experiences with thiophene or thiophene/n-heptane (sulfur content 0.33%, burning light method) show that thiophene cracks to propylene, butane, butene and H_2S, at the same time that 2-methyl-thiophene, 3-methyl-thiophene, di-methyl-thiophene, tri-methyl-thiophene and benzothiophene are formed, being cracking desulfurization the dominant reaction. Hydrogen transfer is an exothermic reaction, thus high temperature limits this reaction. On the other hand, cracking is an endothermic reaction, with high temperatures promoting the same reaction. The fact that 673 K was the optimal temperature for thiophene cracking made the authors conclude that hydrogen transfer is an important elementary step and is involved to saturate thiophene cracking products. The authors suggested however that the desulfurization with cracking of thiophene must be limited by other reactions different than those explained by Saintigny *et al.* (1999) (Figure 6) where hydrogen transfer does not occur.

Based on their experimental results, Shan *et al.* (2002) proposed that thiophene cracks by the following mechanisms:

- Thiophene first obtains a proton on the Brønsted acid sites of USY to form carbonium ion, and then the C–S bond at β position weakens and breaks. The energy of this bond is 268 kJ/mole, the lowest among that of C–H, C–C and C=C. Thus, the thiophene ring opens to form mercaptan species with two double bonds (Figure 8). After carbonium ion isomerization and hydrogen transfer, the remaining C–S bond of the mercaptan at β position breaks, and H_2S and dibutene are produced. Through hydrogen transfer, dibutene can convert to butene and even butane.

- Propylene is also produced during the cracking of thiophene. In the view of Shan *et al.* (2002), the formation of propylene is closely related with the formation of methyl-thiophene. In Figure 8, the mercaptan with two double bonds (from ring opening of thiophene) polymerizes with thiophene. If polymerization occurs at position α (Figure 8), species A is produced. After the carbonium ion isomerization and hydrogen transfer (Figure 9), the C–S bond at position β breaks, and H_2S and 2-butenyl-thiophene are formed. 2-Butenyl-thiophene cracks at β position to produce 2-methyl-thiophene and propylene (after hydrogen transfer). If polymerization between the mercaptan with two double bonds and thiophene happens at β position, species B is formed (Figure 8), and 3-methyl-thiophene is produced following a similar mechanism as described in Figure 9. If thiophene polymerizes with two or three mercaptans with two double bonds at

different positions simultaneously, di- or tri-methyl-thiophene is formed, with however the probability of this event to happen being lower than that of polymerization with one mercaptan. Position α of thiophene is more active than β position, therefore it can be expected that the amount of 2-methylthiophene be larger than that of 3-methyl-thiophene.

- If H_2S is removed from Species A (Figure 8) via β cracking following double bond isomerization and carbonium ion isomerization, 1,3-butenyl-thiophene is formed (Figure 10), and then, benzothiophene can be produced through cyclization of 1,3-butenyl-thiophene
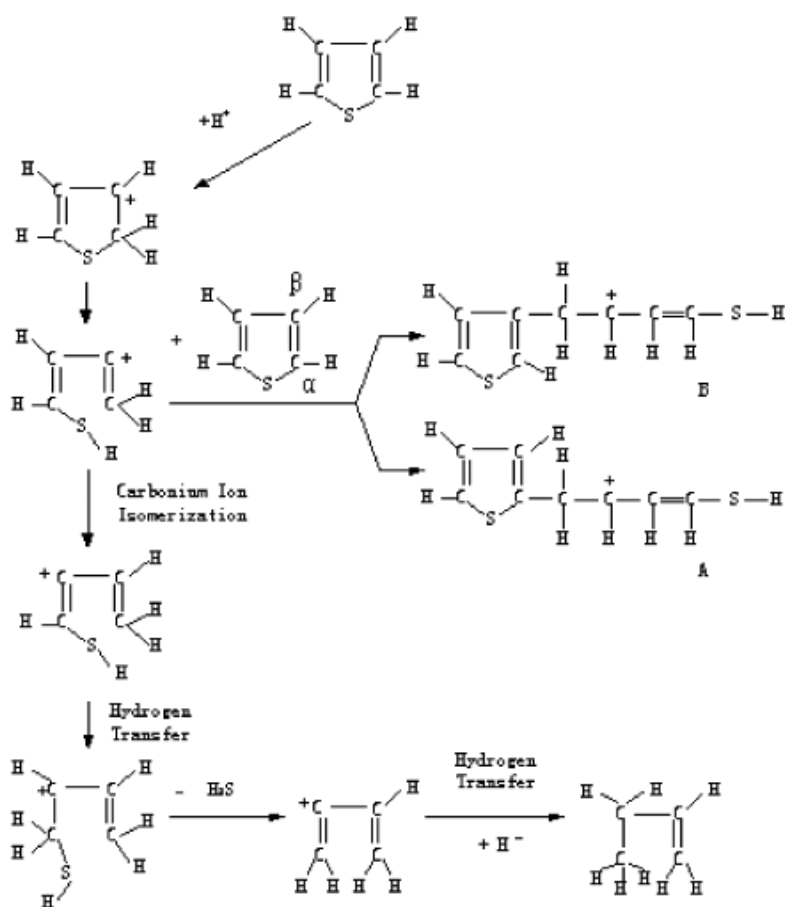
Figure 8. The formation of butene and H_2S in the cracking of thiophene (Reproduced from Catalysis Today, vol. 77, Shan *et al.*, "Mechanistic studies on thiophene species cracking over USY zeolite", p. 117-126, Copyright 2002, with permission from Elsevier).
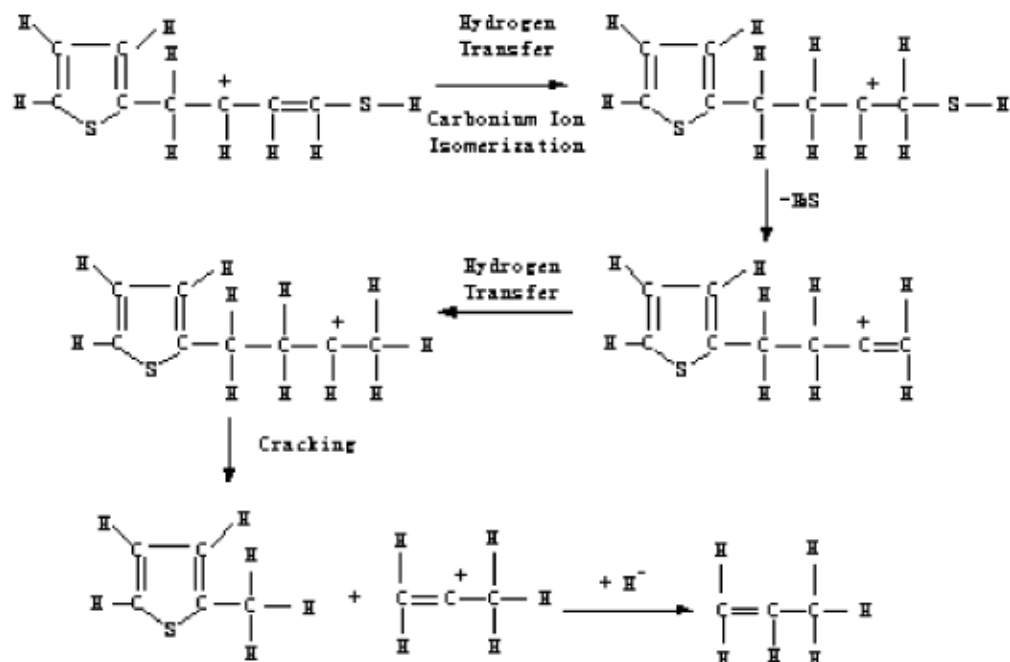
Figure 9. The formation of propylene and 2-methyl-thiophene in the cracking of thiophene (Reproduced from Catalysis Today, vol. 77, Shan *et al.*, "Mechanistic studies on thiophene species cracking over USY zeolite", p. 117-126, Copyright 2002, with permission from Elsevier).
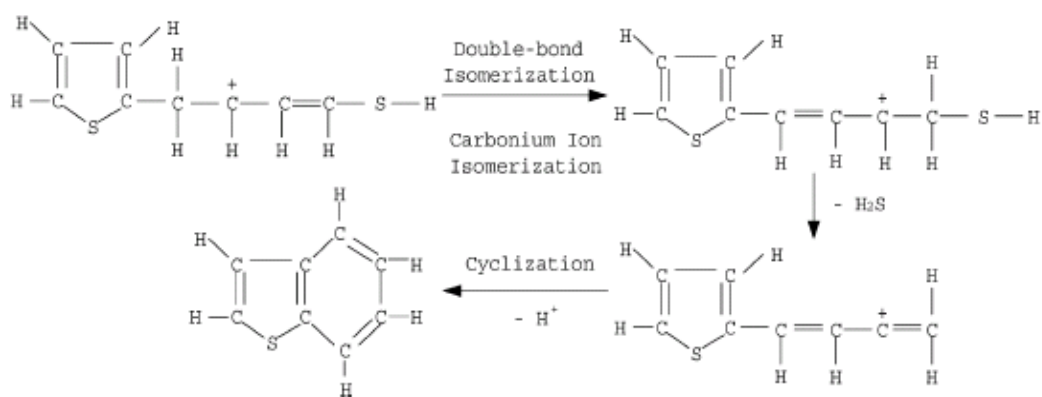

Figure 10. The formation of benzothiophene in the cracking of thiophene (Reproduced from Catalysis Today, vol. 77, Shan *et al.*, "Mechanistic studies on thiophene species cracking over USY zeolite", p. 117-126, Copyright 2002, with permission from Elsevier).

Shan *et al.* (2002) also developed experiments with FCC gasoline distillate over 373 K with a catalyst/oil ratio of 2.5 and reaction temperature of 683 K. They reported a gasoline desulfurization on USY zeolites of 82.5%, however, 60% of the gasoline distillate cracked to light gases. This explains why USY zeolites do not seem to be recommended materials for selective gasoline desulfurization. Their results also show that alkyl-thiophene forms thiophene via de-alkyl reaction, and the alkyl-thiophene conversion increase with the alkyl carbon number.

Another possible pathway to explain the transformation of thiophene into butadiene is via tetrahydrothiophene. Fu *et al.* (2000) argued in their studies, that the formation and decomposition of tetrahydrothiophene was the key step in the decomposition of thiophene, and that the cyclohexane was the best hydrogen donor hydrocarbon in the presence of HY zeolite (compared to n-octane and isooctane). On the other hand, Wang *et al.* (2000) suggested that thiophene firstly obtains hydrogen to form tetrahydrothiophene, and then tetra-hydrogen-thiophene decomposes to produce H_2S. However, Shan *et al.* (2002) did not find tetrahydrothiophene or larger molecules than benzothiophene in their results, making the above hypothesized reaction pathway very questionable.

In spite of the content of mercaptans in gasoline may be low; the catalytic mercaptans conversion becomes pertinent given the principle of catalytic micro-reversibility where the study of a forward reaction is relevant for assessing the backward reaction (e.g. reaction of olefins products of thiophene conversion and H_2S). In this sense, de Lasa *et al.* (2006) evaluated the conversion of ethyl mercaptan (EM) on ZSM5 zeolite without hydrogen addition, using a fluidize bed reactor. They propose that sulfur containing hydrocarbon molecules react over ZSM-5 with a reaction path comparable to the one of their analogous oxygenate species. On the basis of their results, these authors suggest that ethyl mercaptan (EM) is consumed via two competitive reactions, the intra-molecular and the inter-molecular de-hydrosulfidation:

a) *Intra-molecular de-hydrosulfidation.* Ethyl mercaptan reacts via intra-molecular de-hydrosulfidation to give ethylene and H_2S,

$$CH_3 - CH_2SH \leftrightarrow CH_2 = CH_2 + H_2S \tag{1}$$

b) *Inter-molecular de-hydrosulfidation between two mercaptan reacting molecules.* This reaction leads to the removal of H_2S molecule from two mercaptan molecules yielding diethyl sulfide (DiE-S) and H_2S:

$$CH_3 - CH_2SH + CH_2SH - CH_3 \leftrightarrow CH_3 - CH_2 - S - CH_2 - CH_3 + H_2S \tag{2}$$

Moreover, following, this first step, a second reaction step involves further de-hydrosulfidation of diethyl sulfide (DiE-S) yielding an olefin (butene) and H_2S:

$$CH_3 - CH_2 - S - CH_2 - CH_3 \leftrightarrow CH_3 - CH_2 = CH_2 - CH_3 + H_2S \qquad (3)$$
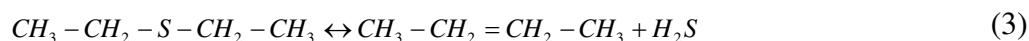
6.1. Sulfur species conversion over zeolites with H donors

Several reports pointed out the importance of hydrogen sources for the transformation of thiophene over acid catalysts. Yu *et al.* (1999) measured thiophene reaction rates in a flow microreactor using C_4H_4S (1 kPa), C_3H_8 (20 kPa)/C_4H_4S (1 kPa), or H_2 (0–200 kPa)/C_4H_4S (1 kPa) reactants, catalyzed by H-ZSM5 at 773 K. They observed that the conversion of thiophene into H_2S was multiplied by 10 when propane (approximately 20 mol/mol) was added to the feed. Their interpretation was that the desulfurization of thiophene occurs through disproportionation (according to Figure 11), as well as through formation of butene and H_2S (see Figure 7), where adsorbed hydrogen atoms or gas phase alkenes formed during propane dehydrogenation reactions provide an alternative path for the removal of the unsaturated hydrocarbons formed during sulfur removal from thiophene.
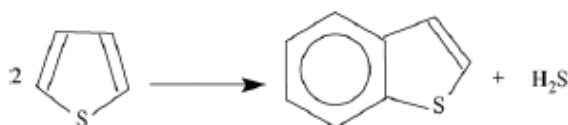

Figure 11. Decomposition of thiophene through disproportionation.

Isotopic tracer studies of thiophene desulfurization reactions were made by the same research group (Li *et al.*, 2001) measuring the chemical and isotopic composition of products formed from ^{13}C-labeled C_3H_8 and unlabeled C_4H_4S mixtures on H-ZSM5; the catalytic reaction measurements were carried out in a glass recirculating batch reactor at 773 K. They concluded that propane–thiophene reactions on H-ZSM5 lead to the formation of aliphatic products (methane, ethene, ethane, propene, and butenes) exclusively from propane, while aromatic products (benzene, toluene and xylenes) contain carbon atoms from both propane and thiophene. Thiophene-derived species do not contribute to the formation of alkenes because they do not enter into alkene oligomerization-cracking cycles. Instead, they react with alkenes to form aromatics that desorb as stable products (Figure 12).
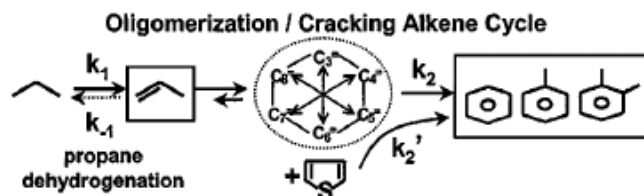
Figure 12. Scheme of the propane–thiopene coupling reaction. Here *k*1, *k*2, and *k´*2 are rate constants of propane dehydrogenation to form propene, aromatics formation from alkene oligomerization-cracking cycles, and aromatics formation from thiopene-derived species, respectively (Reproduced from Journal of Catalysis, vol. 203, Li *et al.*, "Isotopic Tracer Studies of Thiophene Desulfurization Reactions Using Hydrogen from Alkanes on H-ZSM5 and Co/H-ZSM5", p. 175-183, Copyright 2001, with permission from Elsevier).

Later studies were developed by Yu *et al.* (2003) using paraffins as co-reactants in the desulfurization of thiophene catalyzed by H-ZSM5. Catalytic rate and selectivity measurements were carried out at 673 or 773 K using a tubular flow reactor with plug-flow hydrodynamics. Thiophene (1 kPa) was added to a propane–He stream (20 kPa). Thiophene/*n*-hexane (1 kPa/20 kPa) and thiophene/*n*-decane (1 kPa/6 kPa or 12 kPa) reactants were introduced as premixed liquids into a flowing He stream. The two *n*-decane partial pressures (6 and 12 kPa) used were meant to provide a comparison with propane (at 20 kPa) and with *n*-hexane (20 kPa) at their respective equivalent "carbon" (or –CH_2–) partial pressures. All liquid reactants were vaporized immediately upon injection and transferred into the reactor and the analytical system through heated lines kept at 403 K.

The results reported by these authors showed that the co-reactants lead to hydrogen-rich intermediates, which are necessary for the removal of unsaturated fragments formed in thiophene decomposition reactions. It was observed that thiophene desulfurization rates increased along with the increasing alkane chain size, with this showing that the availability of hydrogen-rich intermediates increases with increasing alkane reactivity. Desulfurization rates with alkane co-reactants were significantly higher than those obtained with hydrogen. Sulfur is predominately removed as hydrogen sulfide (>80% S-selectivity) in the presence of alkane co-reactants, but much lower hydrogen sulfide selectivities were obtained when hydrogen was used and thiophene decomposed in the absence of any co-reactant. The presence of thiophene did not alter the nature of the cracking, dehydrogenation, oligomerization, and cyclization pathways typical of alkane reactions or the overall rates of propane conversion on H-ZSM5 (Figure 12). The selectivity for alkane conversion to aromatics, however, increased when

alkane reactions occur concurrently with thiophene desulfurization, indicating that thiophene-derived intermediates contribute to the formation of aromatics by scavenging alkene intermediates formed from the alkane co-reactants. The higher alkene/alkane ratios observed during alkane reactions in the presence of thiophene are consistent with the scavenging of hydrogen-rich intermediates by thiophene-derived species via reactions that form aromatic molecules containing carbon atoms from both alkane and thiophene reactants.

Chica *et al.* (2004) studied rates and selectivities for reactions of adsorbed thiophene on H-ZSM5 and H-Y zeolites, in a packed bed, using O_2, He, H_2, and C_3H_8 streams. These authors reported thiophene adsorption stoichiometries and the identity and yield of products formed during thiophene adsorption at 363 K and during subsequent desorption and reactions at 773-873 K of thiophene-derived adsorbed species. They concluded that thiophene adsorption followed Langmuir isotherms, it occurs with oligomerization on acidic OH group and that the oligomer size depends on spatial constraints within channels. During thermal treatment and using He, H_2, and C_3H_8 as co-reactants, residual thiophene derived species desorb as stable fragments, such as H_2S, ethene, propene, arenes, and heavier organosulfur compounds (methylthiophene and benzothiophene). The product species also form unsaturated organic deposits that cannot desorbed without hydrogenation. H_2 and C_3H_8 remove larger amounts of adsorbed species as unreacted thiophene than He, suggesting that dehydrogenation reactions are inhibited or reversed by a hydrogen source chemical species. C_3H_8 removes as well a larger fraction of thiophene-derived intermediates as hydrocarbons and organosulfur compounds than H_2 or He. Thus, hydrogen atoms formed during C_3H_8 dehydrogenation are more effective in the removal of unsaturated deposits than those formed from H_2. Thiophene derived adsorbed species are completely removed only with O_2 containing streams at 873 K, a process that fully recovers initial adsorption zeolite capacities.

On the basis of these findings it was suggested that the removal pathway of adsorbed species on ZSM-5 zeolite is similar to the proposed by Shan *et al.* (2002) and Saintigny *et al.* (1999). The following considerations are presented:

- H_2S forms at 534 K in He, H_2, and C_3H_8, apparently via ring-opening on thiophene derived species to form unsaturated fragments, a reaction that occurs on Brønsted acid sites via C-S bond cleavage of carbenium ion intermediates (Figure 13 (1)). This process forms H_2S and adsorbed butadiyne species (Figure 13 (3)). On H-ZSM5, desulfurized thiophene fragments are highly unsaturated and unable to desorb as stable molecules without a separate source of hydrogen. Hydrogen transfer must occur for butadiynes (Figure 13 (3)) or ring-opened thiophenes (Figure 13 (2)) to form desorbable species (Figure 13 (4 and 5)). Hydrogen can indeed be provided through adsorbed species formed from C_3H_8 or H_2 or via sacrificial hydrogen transfer from coadsorbed butadiyne species.
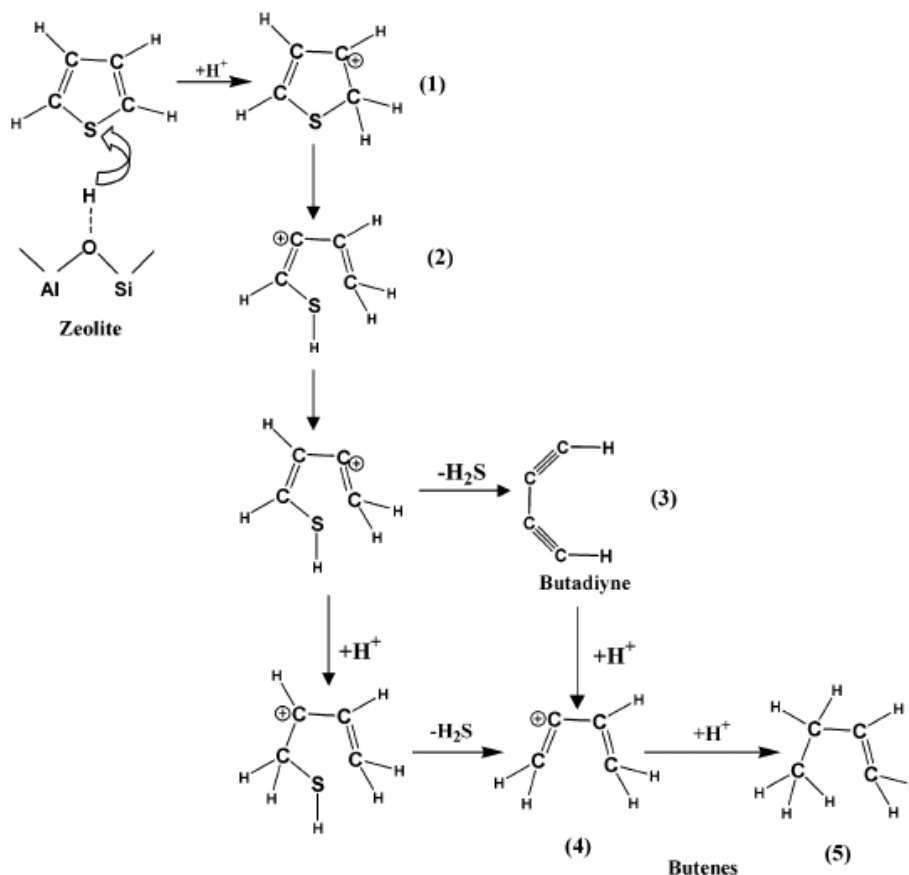
Figure 13. Thiophene ring activation, ring-opening reaction, and formation of H_2S and C_4 fragments (Reprinted with permission from Langmuir, vol. 20, Chica *et al.*, "Adsorption, Desorption and Conversion of Thiophene on H-ZSM5", p. 10982-10991, Copyright 2004 American Chemical Society)

- Benzene forms via hydrogenation of thiophene fragments remaining after ring opening and H_2S evolution. Desorption temperatures and number of evolved benzene molecules resemble those for ethane (730 K and 720 K respectively), indicating that they form via similar steps as ones depicted in Figure 14.
- Propene and methylthiophene evolution profiles are also very similar with desorption temperatures of 670 K and 680 K respectively, suggesting the same connection between them, as it was described by Shan *et al.* (2002) (Figure 9).
- Benzothiophene desorbed in significant amounts at temperatures slightly higher than H_2S (562 K). This experimental finding indicates that benzothiophene

forms as thiophene molecules desorb intact and then react with bound thiophene in the downstream sections of the adsorbent bed via Diels-Alder condensation reactions, forming H_2S and benzothiophene (Figure 11). Benzothiophene could also form via cyclization of adsorbed butenylthiophenes (Figure 10).
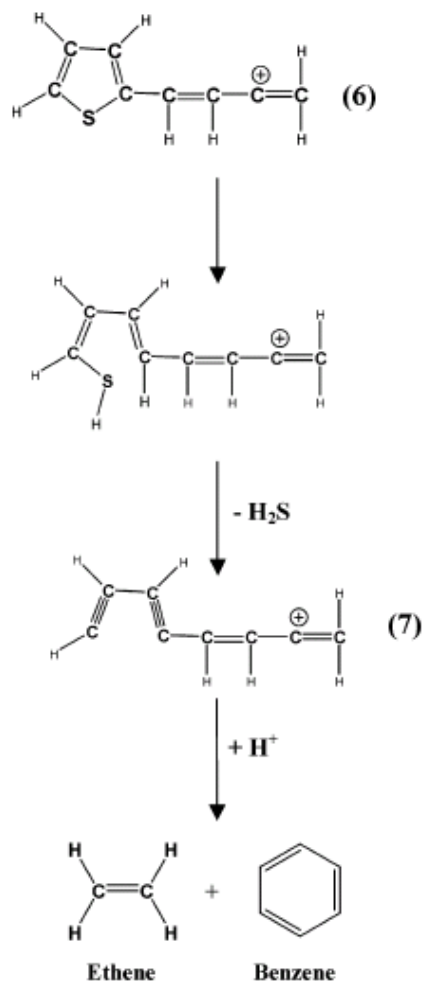

Figure 14. Benzene and ethene formation pathway (Reprinted with permission from Langmuir, vol. 20, Chica *et al.*, "Adsorption, Desorption and Conversion of Thiophene on H-ZSM5", p. 10982-10991, Copyright 2004 American Chemical Society)

7. DETAILED MECHANISTIC INTERPRETATIONS OF SULFUR SPECIES REMOVAL ON ZEOLITES

Sulfur containing species can interact with H-ZSM5 zeolite following a number of reaction steps which will be discussed in this chapter. Based on the literature data, a detailed mechanistic interpretation of sulfur removal on zeolites is proposed.

Studies of adsorption of thiophene on ZSM-5 show that the residual amounts of thiophene derived species after molecular desorption at 773 K correspond to adsorption stoichiometries near unity in all the samples (0.9-1.1 thiophene/Al) irrespective of zeolite structure or Si/Al ratio (Chica *et al.*, 2004).
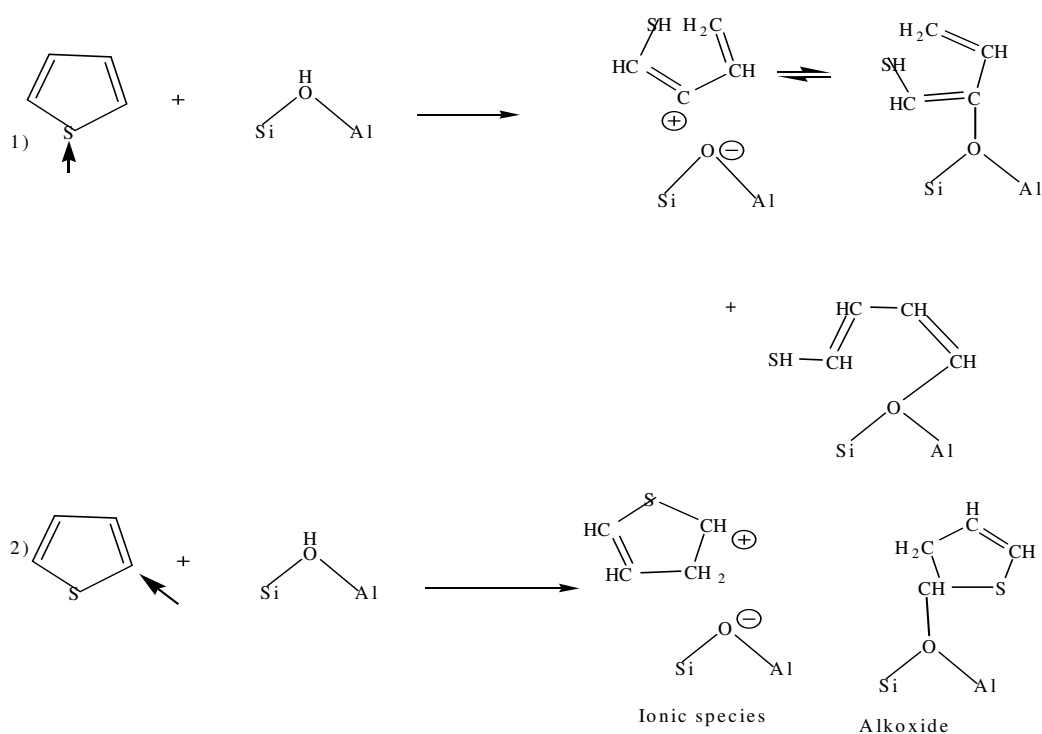

Figure 15 Adsorption of thiophene in ionic or alkoxide species leading to 1) Ring opening with formation of the adsorbed sulfur butadienyl group 2) No ring opening

The reported data indicate that these residual thiophene derived species are associated, as show in Figure 15, with specific irreversible interactions between thiophene and the surface acidic OH groups. These thiophene adsorbed species (e.g. sulfur butadienyl species) can undergo further reactions. The ionic species on

the surface can be considered transition states with the alkoxide species intermediates (refer to Figure 15).
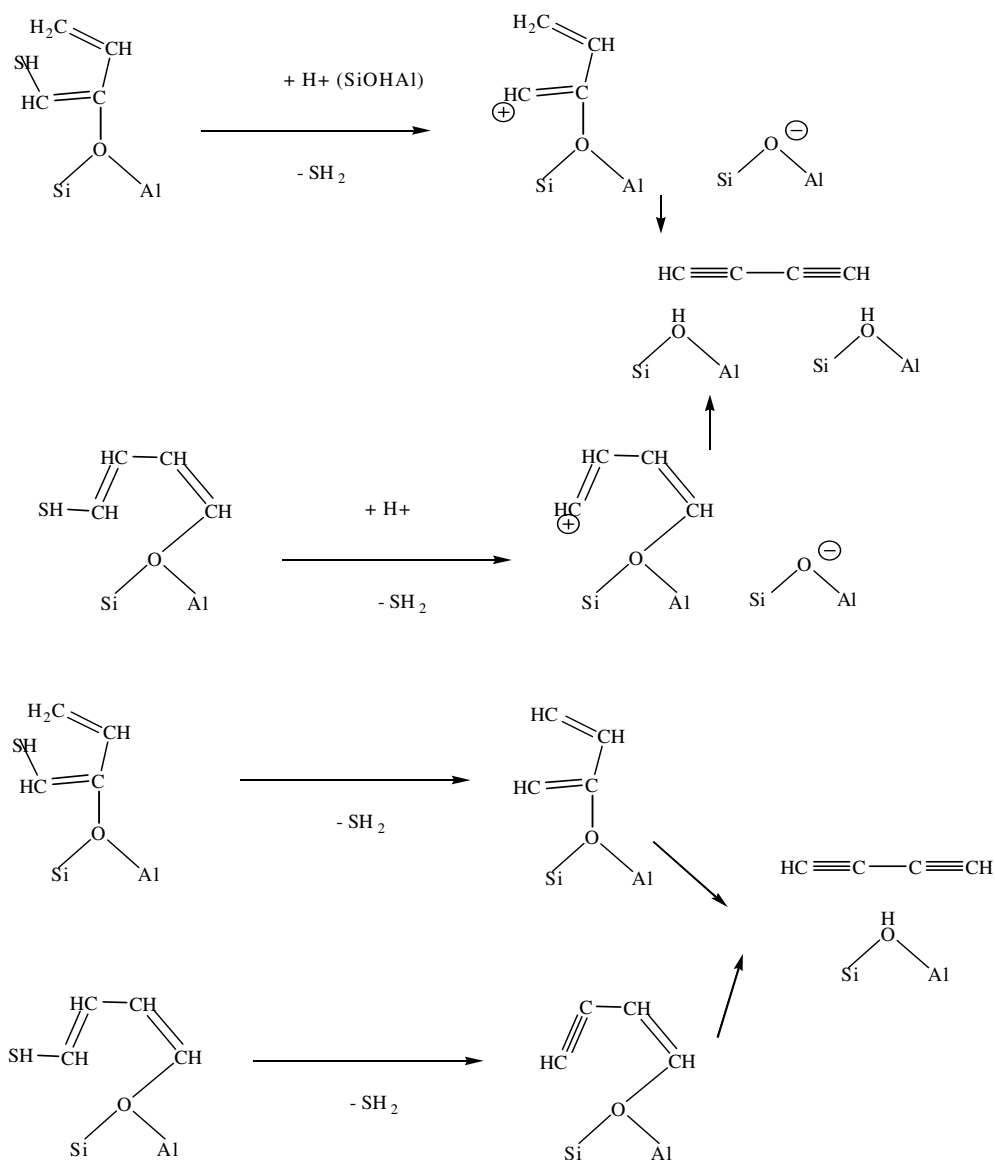

Figure 16. Conversion of the adsorbed sulfur butadienyl group into Butadyine

Ferreira's research group, considering literature data, proposes a number of mechanistic interpretations for the conversion of the key adsorbed hydrogen sulfur butadienyl intermediate:

a)   Unsaturated residues desorb only from H-ZSM5 via hydrogenation using sacrificial co-adsorbed species (in He), or external H sources (H_2, propane) or via combustion pathways (vis-O_2). Thermal treatments led to the formation of H_2S, ethene, propene, benzene, toluene, methylthiophene, and benzothiophene as the predominant products following published reports from Chica *et al.* (2004). Figure 16 shows the progress of the reaction of butadyine formation.

b) H_2S forms at 534 K under He, H_2 and propane carriers. Figure 17 provides a possible explanation of the hydrogen sulfide formation from the adsorbed hydrogen sulfur butadienyl species described in Figure 15. Thus on H-ZSM5 desulfurized thiophene fragments are highly unsaturated and unable to desorb as stable molecules without a separate source of hydrogen.
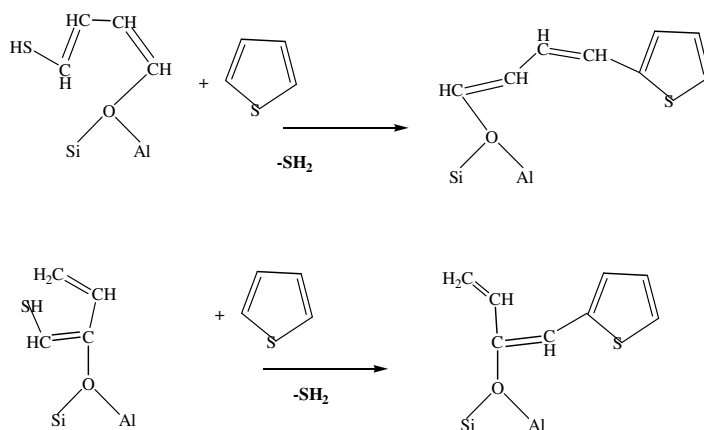

Figure 17. Reaction of the adsorbed sulfur butadienyl group with Formation of hydrogen sulfide

c)   Hydrogen transfer must occur for butadyines or ring opened thiophenes to form desorbable species. Hydrogen can be provided through adsorbed species formed from propane, or H_2 via sacrificial hydrogen transfer from co-adsorbed butadyine species. The type of mechanism explains the formation of ethylene (Figures 18 and 19). The benzene evolution occurs immediately upon heating pre-adsorbed thiophene above room temperature. This implies that benzene forms via hydrogenation of thiophene fragments remaining after ring opening and H_2S evolution (Figure 20). Propylene and methylthiophene seem to be formed through the similar adsorbed sulfur butadienyl intermediary species as ethylene and benzene (Figure 21).
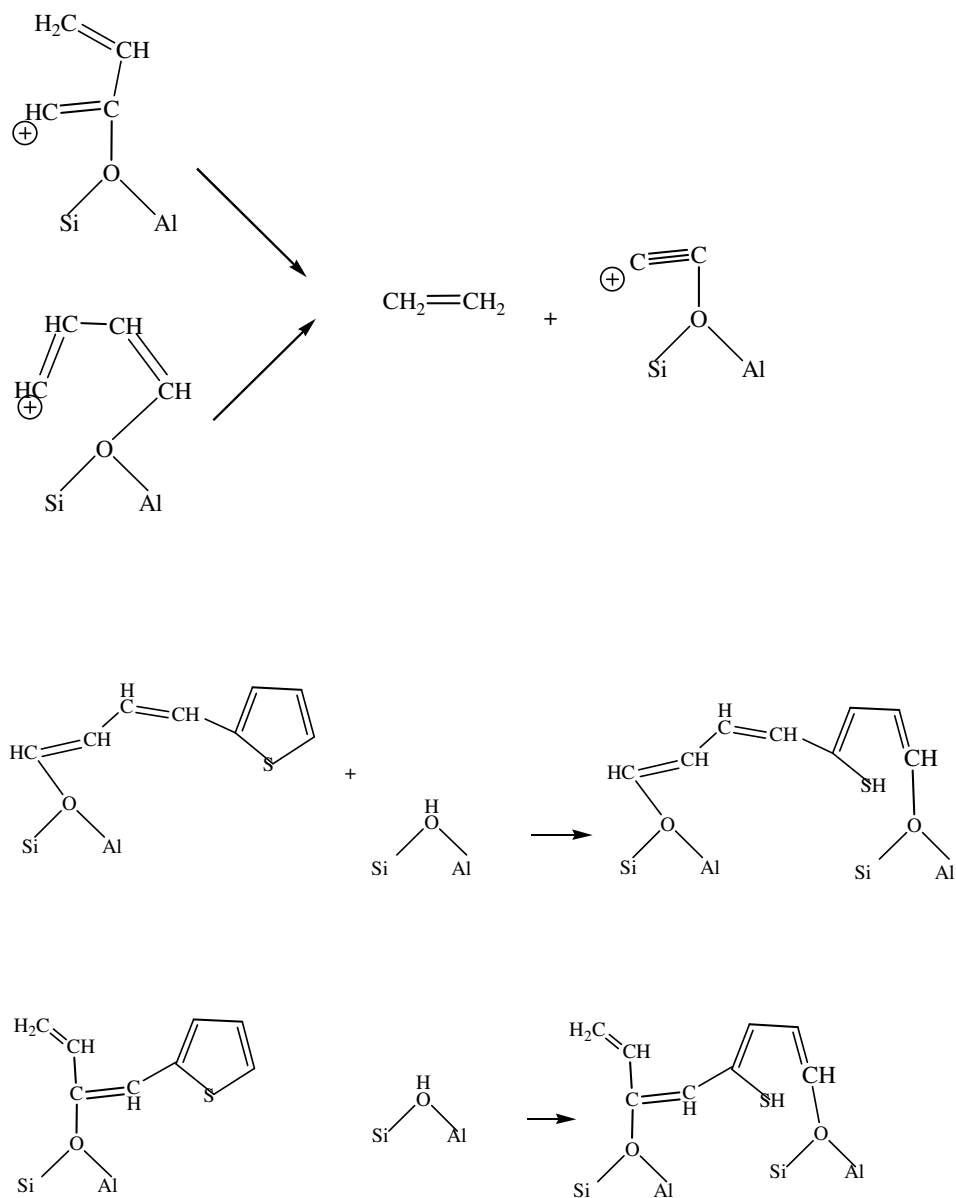
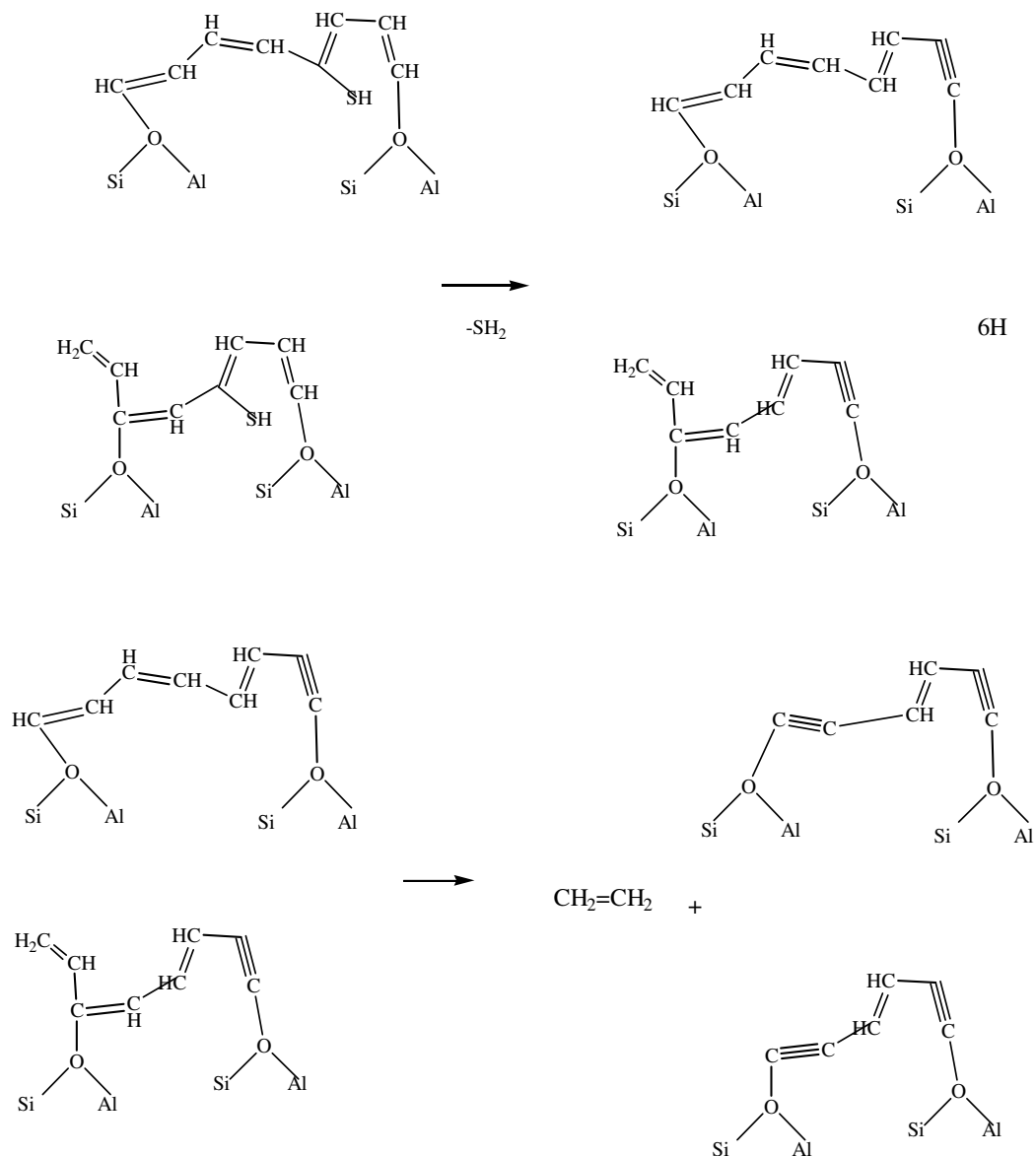Figure 18. Conversion of adsorbed butadienyl and sulfur butadienyl species with formation of ethylene

Figure 19. Formation of ethylene via the reaction of two adsorbed neighbor thiophene derived species
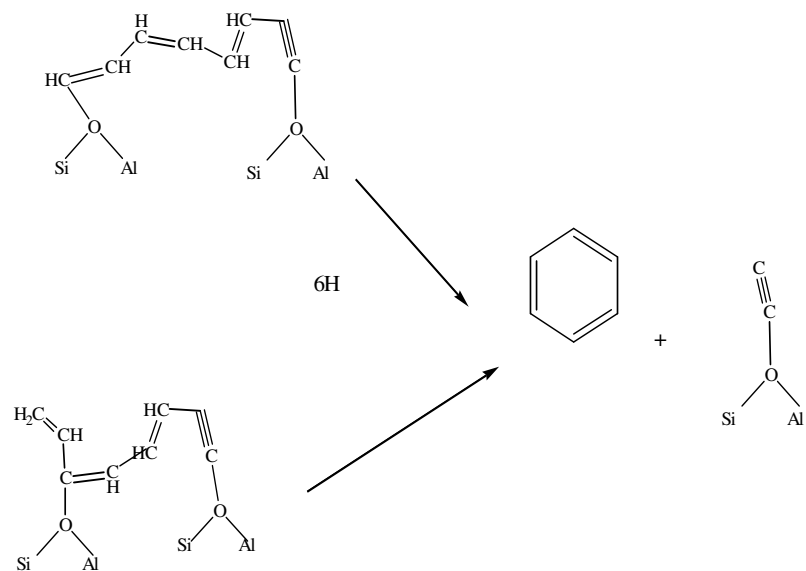
Figure 20. Formation of benzene under H_2 from two adsorbed neighbor thiophene derived species
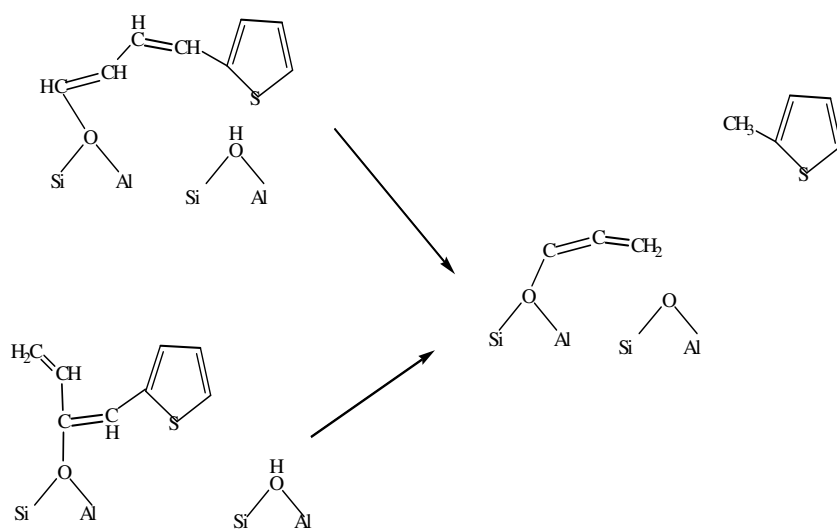

Figure 21. Formation of methyl-thiophene from alkyl substituted thiophene species

7.1. The sulfur-butadienyl group as a key intermediate in sulfur removal and H₂S, ethylene, propylene, benzene and methyl-thiophene formation.

The adsorbed sulfur butadienyl intermediary, formed by reaction of thiophene with desulfurized residues on the surface, can suffer cracking and cyclization or reordering and hydrogenation. Iglesia's research group (Yu *et al.* 1999 and 2003, Li *et al.* 2001, Chica *et al.* 2004) considers that this is influenced by the availability of H⁺. However, Ferreira´s research group argue about a mechanism based on the experimental facts explained above: a) the existence of Al-Al Brönsted "pairs" on the surface of ZSM5 separated by 5.5 to 8 Å, b) the formation of methylthiophene and propylene from the butenyl thiophene (Figure 21), c) the formation of benzene or ethylene from the desulfurized butenyl thiophene (Figures 18 to 20), d) the formation of ethylene from the butenyl residue of the thiophene after desulfurization, e) the formation of propylene from the thiophene adsorbed on the surface (described in Figures 22 to 24), and f) the formation of benzothiophene through reaction of the residue C4 with another thiophene molecule by a Diels Adler reaction (refer to Figure 25). Benzothiophene can be produced in an isolated Brönsted site or involving pairs of Brönsted sites.
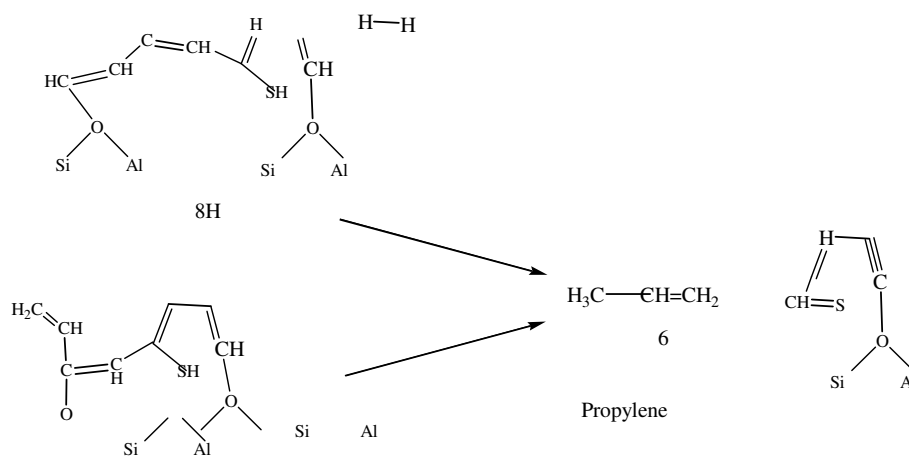

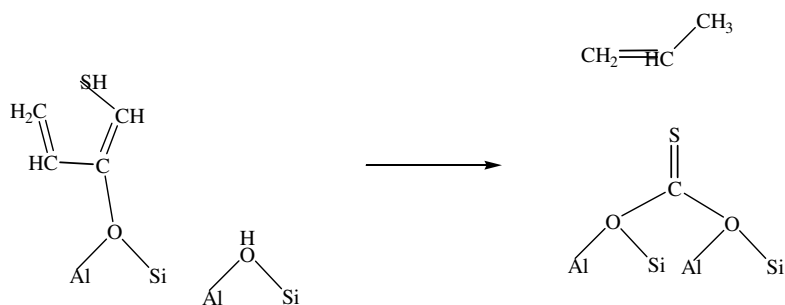Figure 22. Propylene formation from two adsorbed neighbor derived species

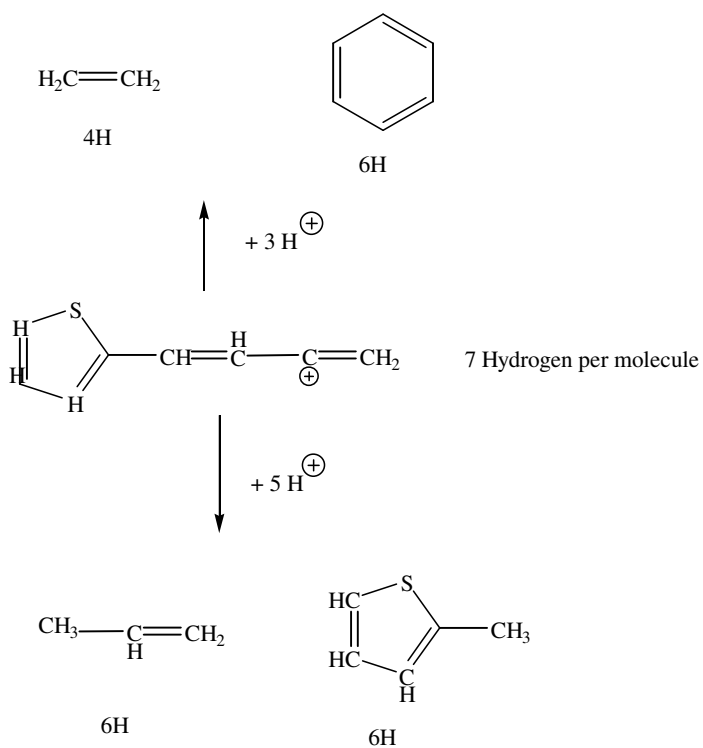Figure 23. Propylene formation from one adsorbed derived species

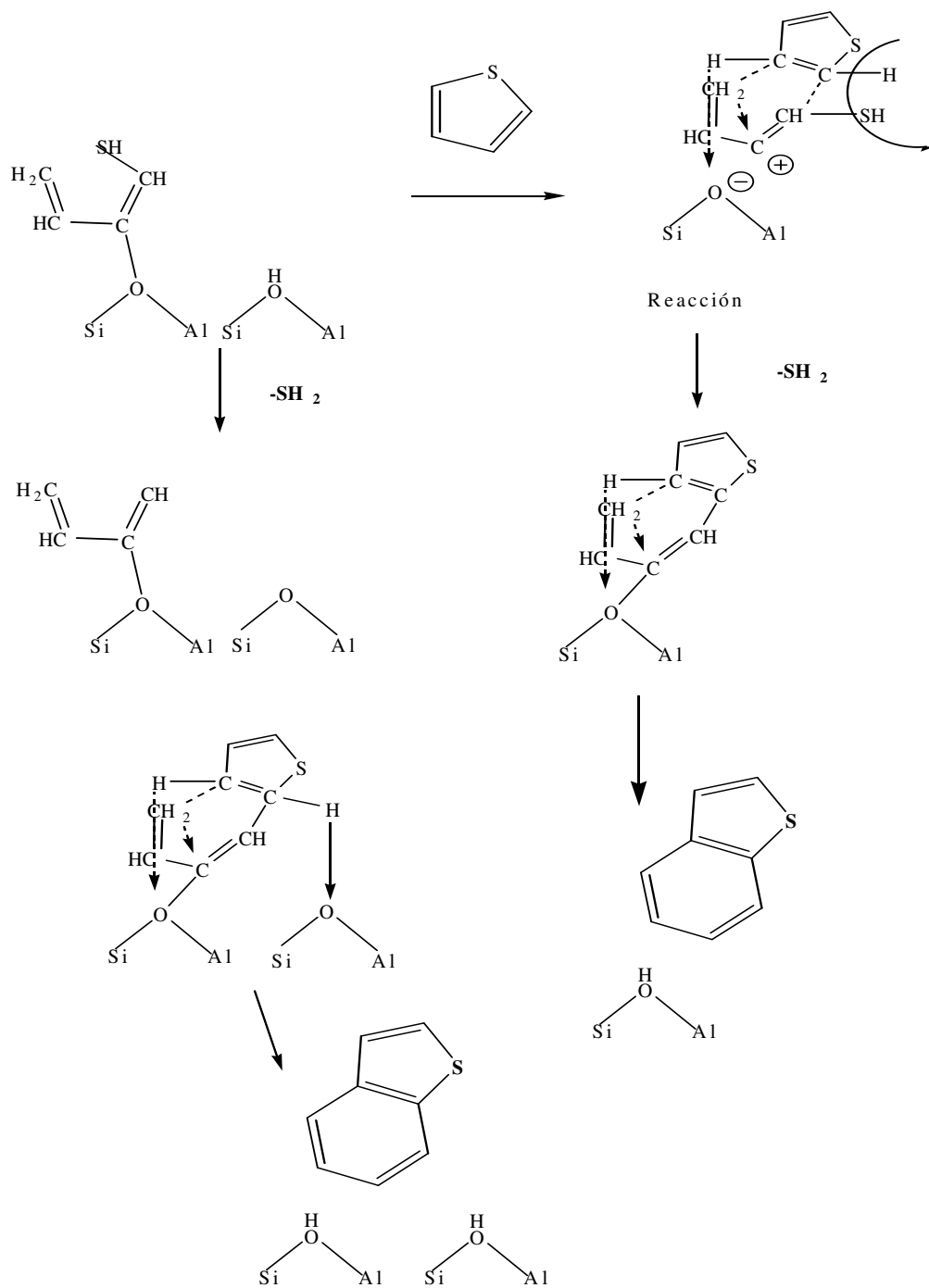Figure 24. Further hydrogenated surface species

Figure 25. Benzothiophene formation from a thiophene and an adsorbed thiophene derived specie

When there is a severe deficiency of hydrogen, the tendency would be then to form ethylene and benzene. Even more when more hydrogen is available in the neighbor sites of the adsorbed species with 6-7H per molecule, the formation of propylene and methylthiophene would be preferred. Toluene and benzene, C_5 and C_6-non-aromatics compounds can be formed also by reaction of C_4 residues with evolved ethylene and propylene. Methane can result from the propylene decomposition on acidic sites on ZSM5 (see Figures 22 and 23). The results of Iglesia´s research group (Yu *et al.* 1999 and 2003, Li *et al.* 2001, Chica *et al.* 2004) show that with He or H_2, ethylene and benzene are favored; whereas with propane available, relatively more propene and toluene are formed (see Figure 24). Dimerization of thiophene can also take place as described in Figure 26.
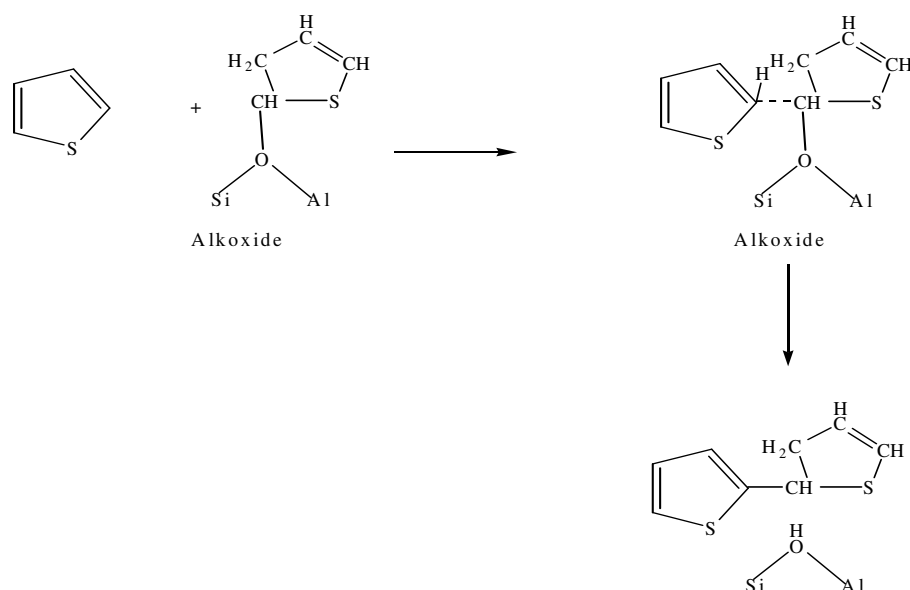
Figure 26. Dimerization of thiophene and a thiophene adsorbed specie

7.2. The Brönsted and Lewis sites

In the case of zeolites, one of the least studied phenomena is their basicity under dehydrated conditions. The dehydration/dealumination process generates both acidic Brönsted sites but also Lewis acid and Lewis basic (LB) sites. In the case of Brönsted sites, it is apparent that they can be traced to the OH groups from AlOHSi, with the Basic Lewis sites being the result of O in the framework of AlO_4 species, and the Lewis acidic sites Al^{+3} (of low coordination) or Si^{+4} of low coordination and low symmetry. The zeolite oxygen basicity arises from the

presence of negatively charged AlO_4 tetrahedra, a chemical state that not only can take place during the preparation, but also under reaction conditions given the proton-donating step and dehydration. The basicity in the non-protonic forms of zeolites arises from Al in the species $AlO(SiO)_aAlO$ with a=1 yielding strong basic site and a=2 medium given to weak basic site. Besides the Al concentration, the connectivity of T sites is a parameter to consider.
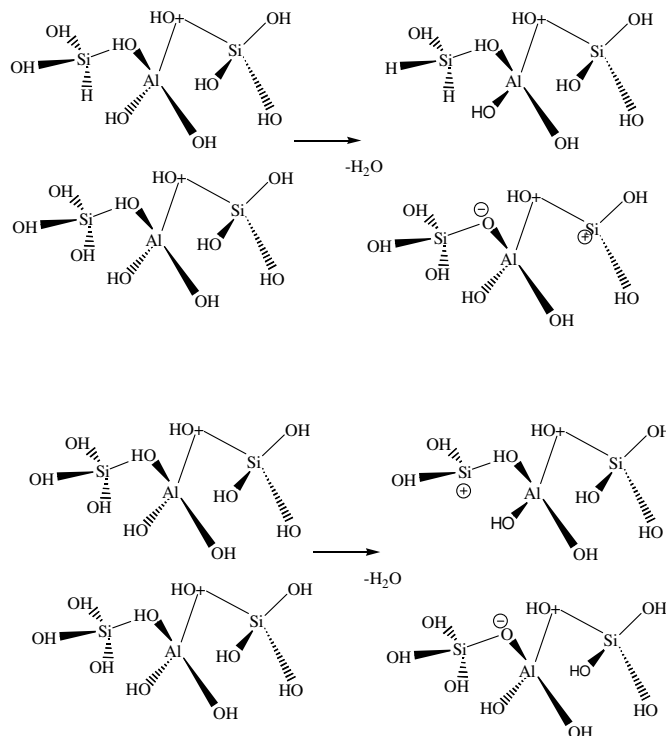
Figure 27. Formation of Brönsted acidic sites, Lewis basic sites and Lewis acidic sites on Zeolites

Brandle and Sauer (1998) concluded that the basicity sequence of relatively high silica frameworks is MOR>MFI>CHA>FAU. The acidity follows the inverse sequence for these authors. Bartholomeuf (2003) found that zeolite frameworks induce basicity through their topologies. Basicity increases with Al amount. However, the series of topological density FAU<LTL<BEA<MWW<MOR<MFI<FER is opposite to that proposed by Brandle and Sauer (1998) and more related to the experimental work. The presence of H^+ as a particular kind of cation is important to understand the remaining Lewis basicity of the O bonded to Al in the framework. For a given

zeolite framework and Si/Al ratio the basicity increases in the series as follows: $Li^+<Na^+<K^+<Rb^+<Cs^+$ and $Mg^{+2}<Ca^{+2}<Sr^{+2}<Ba^{+2}$. Being H^+ the cation, the Lewis basicity of the O bonded to the Al can be part of the active site. Figure 27 reports how Lewis acid and basic sites are formed upon dehydration, beyond the Al per Si substitution. After proton donating the acidic OH it leaves a very weak base, with the other oxygen bonded to the Al being a stronger base given the imbalance in basic strength. Complex reactions can also be taking place when the catalyst is exposed to thio species (see Figure 28).
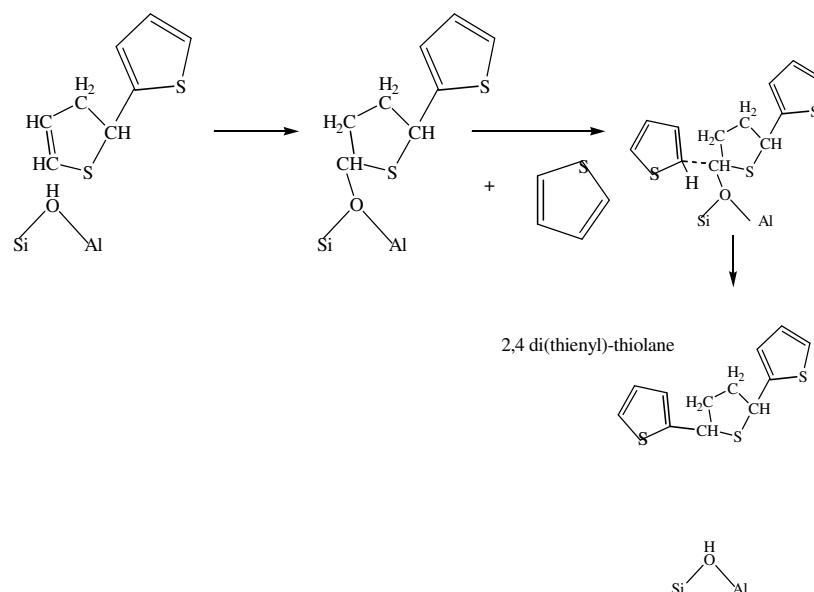
Figure 28. Formation of 2,4 dithienylthiolane

Lewis basic sites and its presence on zeolite surface are important to be considered to understand, for instance, the dimerization of thiophene (refer to Figure 29). The hydrogen beneficial effects can be assigned to the generation of new O-H groups bonded to Si and Al during the reaction and upon hydrogenation.

The presence of Brönsted acid H-Lewis basic oxygen pairs can also explain the easy formation of benzene and H_2S at low temperatures using silica alumina catalysts (see Figure 30).

One can notice that the formation of the species highlighted with a in the Figure 30, are supported by the FTIR findings of Yu *et al.* (2003) with CH_2-C=C bonds detected on the surface after adsorption of thiophene at low temperature.
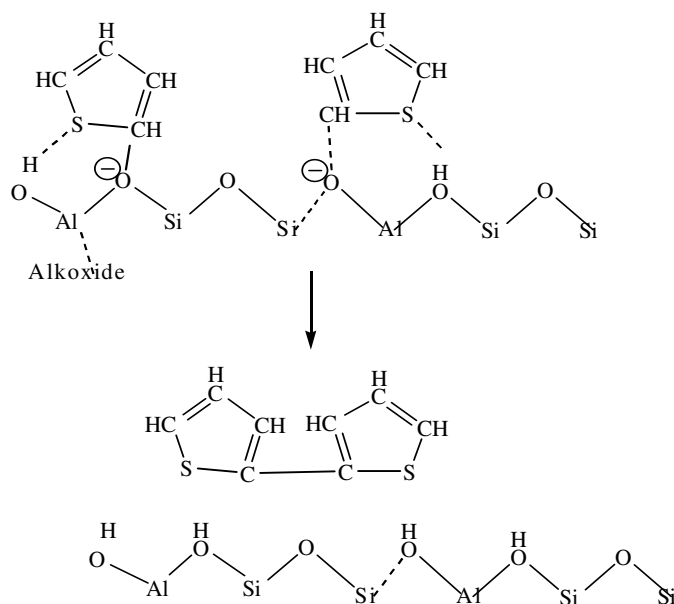
Figure 29. Role of basic Lewis Oxygen in dimerization without hydrogenation
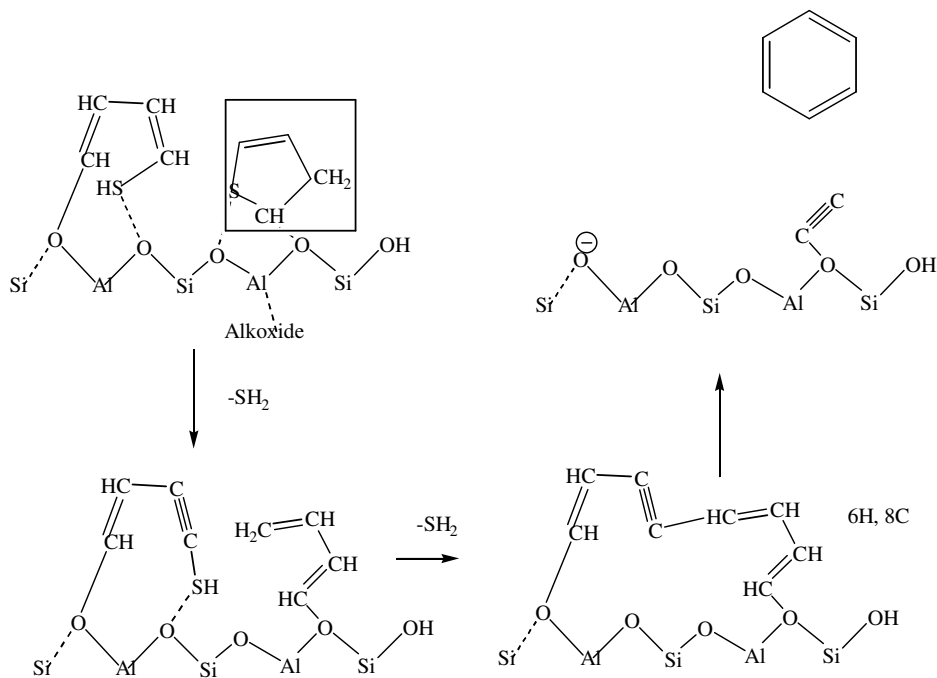
Figure 30. Formation of Benzene and H₂S

7.3. Alkoxide versus carbocation character

Recent studies on the adsorption over H-ZSM5 and protonation of propene, 1-hexene and 3-hexene demonstrated that these zeolites covalent alkoxide intermediaries. Bhan *et al.* (2003) found the formation of a physisorbed π-complex involving the olefin double bond and the acidic proton to be relatively independent of olefin structure and site geometry. However, they show that the proton transfer process for the formation of a covalent alkoxide intermediate involves a carbenium-ion like transition state, with an activation energy that is dependent on the protonation site of the olefin and relatively independent of the carbon number and double bond location at the olefin. Accessibility of the alkoxide oxygen site in the cavity plays a significant role in the stability of the alkoxy species. The overall energy of alkoxides adsorption depends strongly on the crystallographic Al site and the specific host oxygen for the Brönsted proton. Primary and secondary alkoxides species have a comparable stability within the zeolite cavity. Changes in the zeolite structure can affect the energy of alkoxide formation dramatically. The authors observed coordination between multiple oxygens attached to the Al at the TS geometry. Olefin protonation mechanism does not involve the bifunctional acid base nature of the zeolite with an activation energy that is comparable to bifunctional mechanism (Bhan *et al.*, 2003).

8. THIOPHENE REACTION ON ZEOLITES AS DESCRIBED WITH MOLECULAR SIMULATION

The acid-catalyzed reactions are not in general well understood. The theoretical study of desulfurization reaction paths of sulfur containing molecules after contact with Brönsted acid sites (BA) will also provide a basis to a better understanding of the reactivity of such sites at the molecular level. Thiophene has been used as a model compound because it is the smallest sulfur containing and aromatic molecule.

Saintigny *et al.* (1999) presented the study of desulfurization of thiophene upon contact with acidic zeolite using the DFT method. Two different mechanisms have been compared occurring in the absence or presence of hydrogen. The presence of hydrogen does not affect the activation barriers, but changes the overall enthalpy of the reaction. The reaction of thiophene to produce butadyine and H_2S is thermodynamically unfavored (ΔG =263 kJ/mole, ΔH=313 kJ/mole), whereas in the presence of H_2, the formation of butadiene is exergonic, with values of -24 to -40 kJ/mole. One of the points to consider is the adsorption energy of the thiophene molecule. Experimental values are close to -60 kJ/mole. However, thiophene adsorption in its two forms presents -15 kJ/mole from

theoretical studies with this discrepancy assigned to the model considered for the calculations of DFT.

The model used for DFT calculations (see Figure 31) involves Al tetrahedral, with 2 OH. This is similar to a Brönsted site in hydrated ZSM5, but not to a dehydrated one, when Lewis Acidic and Lewis Basic sites are also present, besides dealumination. However this model has been used consistently in all the published studies (Saintigny *et al.* 1999, Bratholomeuf 2003). The dehydrated ZSM5 studied experimentally by NMR presents 2 different kinds of Al, which has been assigned to tetrahedral environments.
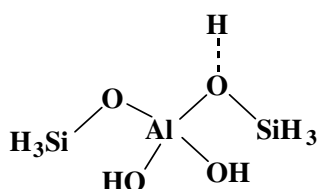
Figure 31.Model considered for calculations-Hydrated ZSM5

A recent manuscript by Elanany *et al.* (2005) reports that the active sites responsible for the superacidity of dealuminated zeolites are thought to arise from the interaction of EFAL Lewis acid sites with Brönsted sites. These authors studied $Al(OH)_2^+$, AlO^+ Si^+ and Na^+ as Lewis acidic sites in mordenite. They concluded that both AlO^+ and Si^+ can contribute to the generation of superacidity. In Figure 32 different kinds of Aluminium EFAL are shown. Al atoms involved in terminal structures and also in dimmers through O with the general structure $(AlO_2H)_2$ are examples of EFAL.

The possibility of a strong Lewis acid coupled with a very acidic Brönsted acid was proposed for ZSM5 dehydrated several years ago (Gates *et al.*, 1979). DFT studies by Saintigny *et al.* (1999) showed transition states for thiophene reaction with activation energies as high as 300 kJ/mole. Reaction enthalpies near 150 to 300 kJ/mole were reported for free of H_2 atmospheres, while enthalpies near +13 kJ/mole were observed with H_2 being present. However, this DFT study underestimated the thiophene adsorption energy. The authors considered that the contribution of the micropores or the "docking energy" was needed to resemble the adsorption energy. However, one of the issues is that the active site cannot be isolated enough to represent the single thiophene adsorption event on dehydrated ZSM5. Rozanska *et al.* (2001) reported a DFT study of the cracking reaction of thiophene by small zeolitic cluster catalysts. These authors argue that cracking of thiophene is catalyzed by Lewis basic oxygen atoms. On this basis a new model of acidic sites in ZSM5 was reported.
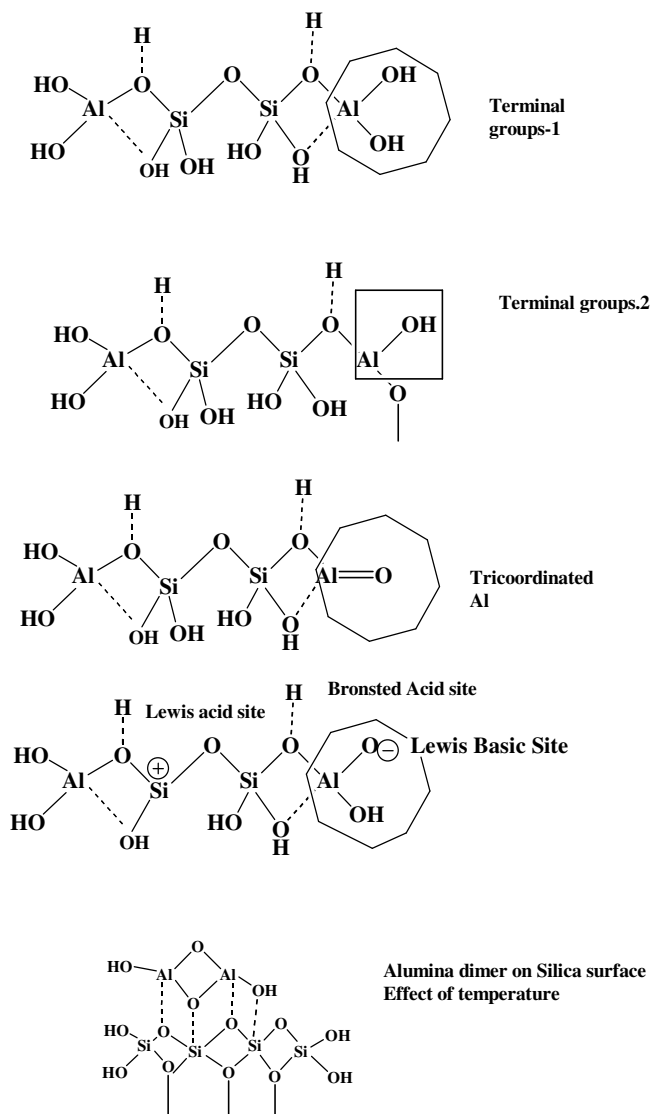
Figure 32. Pairs of sites involving Al with different neighbors- Dehydrated ZSM5

It has been shown that prehydrogenation of thiophenic aromatic species greatly enhances the desulfurization reaction rates (Rozanska *et al.*, 2001). Under these conditiones, the Brönsted acidic site indirectly participates in the controlling reaction. On this basis, it is speculated that the acidity of zeolite is not a key factor. Rozanska *et al.* (2001) also used in their analysis a 3TOH site model. They found that H_2O and H_2S decrease the thiophene cracking activation energy. However, both of these molecules are recognized poisons to the catalyst. The prehydrogenation of thiophene almost does not change the activation energy for

the reaction. Nevertheless, the stabilization energy for the final alkoxy species formed from the prehydrogenated thiophene changes by -40 kJ/mole and this when compared with the stabilization energy of the alkoxy species generated from the non-prehydrogenated thiophene. As these authors used cluster models of the zeolite catalyst in their theoretical calculations, they could only provide qualitative trends.

Vrinat *et al.* (1980) and Ono *et al.* (1980) reported that proton-exchanged zeolites are not the most efficient catalysts in thiophene and dibenzothiophene cracking, zeolites with stronger Lewis basic sites showing a faster reaction rate.

A recent study from van Santen´s research group (Saintigny *et al.* 1999, Rozanska *et al.* 2001 and 2003) showed that thiophenic ring cracking is the rate-limiting reaction-step in thiophene and benzothiophene hydrodesulfurization. The authors used periodic electronic DFT calculations of thiophene, dihydrothiophene and dibenzothiophene cracking catalyzed by proton and lithium-exchanged mordenite. London forces were assumed to be approximately constant on intermediate and transition states, whereas zeolite electrostatic and repulsion forces dramatically altering the species-surfaces interactions (Rozanska *et al.*, 2003). On this basis it was considered that the protonation step as the first step cannot provide a proper description of chemical events, with the attack of oxygen as a Lewis basic site being the true active site. In this sense the H^+ acts as a stabilizer only. Activation energy for cracking was assessed at 318 kJ/mole. This leads to the formation of alkoxy specie which is favored by +128 kJ/mole and this with respect to the physisorbed thiophene. One should be notice that the activation energy of thiophene cracking by Li-exchanged mordenite is 280 kJ/mole. This energy is 38 kJ/mole lower than the activation energy for the proton exchanged mordenite in the periodic calculation. As a result, these authors consider that Li exchanged zeolites can more easily induce thiophene changes than proton exchanged ones s. As a result the authors reach at several conclusions on important issues:

a) Stabilization of a given transition-state complexes is dependent on the size of the zeolite cavities.

b) When the extent of charge separation in the transition-state is not adequate, the zeolite becomes destabilized. Other factors such as the size of the transition structures and the number of H atoms in the hydrocarbon molecule are very important, as well as the zeolite micropore dimensions.

c) The zeolite framework has a consequent stabilizing effect of carbocationic transition states in the conversion of aromatics or olefin chemisorption.

d) The thiophenic derivative cracking activation energies are in the range 270-320 kJ/mole. These are higher by 30 kJ/mole than those experimentally measured when metal sulfide(s) catalysts are used.

This new type of site will mainly change the first step (the adsorption) and the cracking step that is the controlling one. After the complete alkoxide formation, the site influence is almost lost and then the observed behavior is similar for the different model sites. The ensuing reactions can be related to the surface reactions of the alkoxide formed with the zeolitic structure affecting the transition-state of dihydrothiophene and of benzotiophene and derivatives mainly, given steric reasons.

Figure 33 shows the species of thiophene on LA-BA-LB complex sites. Using PM3, the activation energy through an ionic state presents and activation energy of 313 kJ/mole, whereas the final state is 45.2 kJ/mole more endothermic. DFT methods are theoretically much more precise in terms of comparison with experimental results, especially if electronic effects are significant in the reaction. In spite of this, the PM3 provided, for the selected reaction, an activation energy value very close to the experimental one.
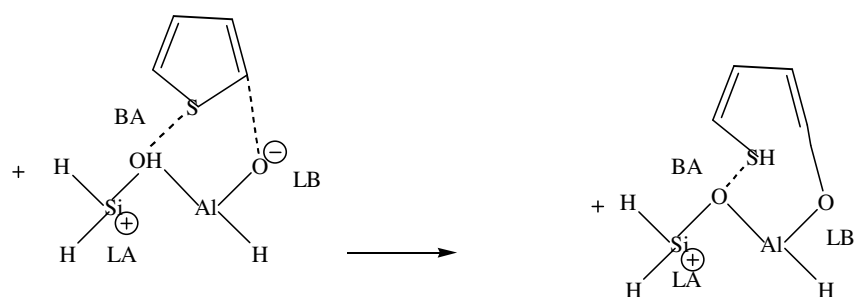
Figure 33. Species of thiophene on Lewis Acid (LA)- Brönsted acid (BA)-Lewis Basic (LB) complex sites

Xu *et al.* (2006), Richardeu *et al.* (2004), and Tonetto *et al.* (2004) developed theoretical studies using thiophene as probe molecule. Their considerations are valid for all zeolites locally. However, the micropore size and the Si/Al ratio are very important in terms of distribution of Brönsted acidic sites, Lewis basic and Lewis acidic sites. In this sense, ZSM5 seems to be selective for thiophene, whereas other zeolites allow the introduction of the bigger molecules in cavities, having then access to EFAL sites. If the zeolite framework is not well suited to favor zwitterionic transition state complexes (Figure 34), more favorable conditions can be met to allow competitive zeolite based hydrodesulfurization. Chemical modifications of the zeolites with selected molecules could produce the needed conditions for the desired reactions.
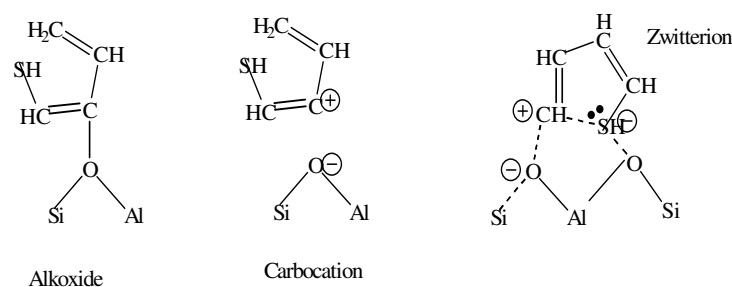
Figure 34. Comparison between alkoxide, carbocation and zwitterion structures

9.   THERMODYNAMIC   ANALYSIS   OF   SULFUR   SPECIES CONVERSION OVER ZEOLITES

As described in the previous sections, it appears that ethyl mercaptan conversion involves intra-molecular and inter-molecular de-hydrosulfidation. de Lasa *et al.* (2006) considered these reactions in the context of thermodynamics equilibrium to formulate chemical equilibrium calculations. Hysys, a Hyprotech commercial process simulator software, was used to aid in equilibrium constant and equilibrium composition calculations of the proposed set of three simultaneous reactions for the de-hydrosulfidation of ethyl mercaptan, named in section 6 as equations (1), (2) and (3). Calculations were carried out using the same operation conditions (temperature, pressure, reactant concentration) used during their experimental studies.

The chemical equilibrium constants for the three reactions calculated by de Lasa *et al.* (2006) are reported in Table 4. Reactions 1 and 3 are endothermic reactions while reaction 2 is exothermic. All equilibrium constants were higher than one, thus all three reactions were considered thermodynamically favored under the selected operating conditions.

Regarding the three reactions involved, reactions 1 and 2 are of the competitive type while reactions 2 and 3 are in series. Thus, the authors concluded that the overall reaction scheme of de-hydrosulfidation is of a combined parallel-in series reaction network with three reactions contributing to the product distribution.

Furthermore, observing the equilibrium constants calculated at the temperature range studied, the equilibrium constants for reaction 1 (K1) are consistently higher than the equilibrium constants for reaction 2 (K2), and the equilibrium constants for reaction 3 (K3) are much larger than the ones for both reactions 1 and 2. This showed that there is no thermodynamic restriction for diethyl sulfide species formed to be consumed completely. In this respect,

calculated equilibrium conversions, at least 99% in all cases, confirmed that these reactions were not equilibrium limited.

Table 4. Equilibrium constants in the 623-773 K temperature range for the EM de-hydrosulfidation reactions (equations 1, 2 and 3) (de Lasa *et al.*, 2006).

T [K]	K_1	K_2	K_3
623	4.4	3.0	412.7
648	8.1	2.9	695.0
673	14.7	2.8	1136.2
698	25.4	2.8	1808.8
723	42.8	2.7	2811.9
748	70.0	2.7	4278.6
773	111.7	2.6	6385.6

de Lasa´s research group developed other extensive thermodynamics analysis, not published yet, that takes into consideration all the possible reactions of thiophene conversion over zeolites, proposed in the theoretical and experimental studies described in section 6. A set of reactions in presence and absence of hydrogen was studied under equilibrium conditions. It is expected that this approach allows identifying the reactions most thermodynamically favored. The set of reactions evaluated is shown in Figure 35.
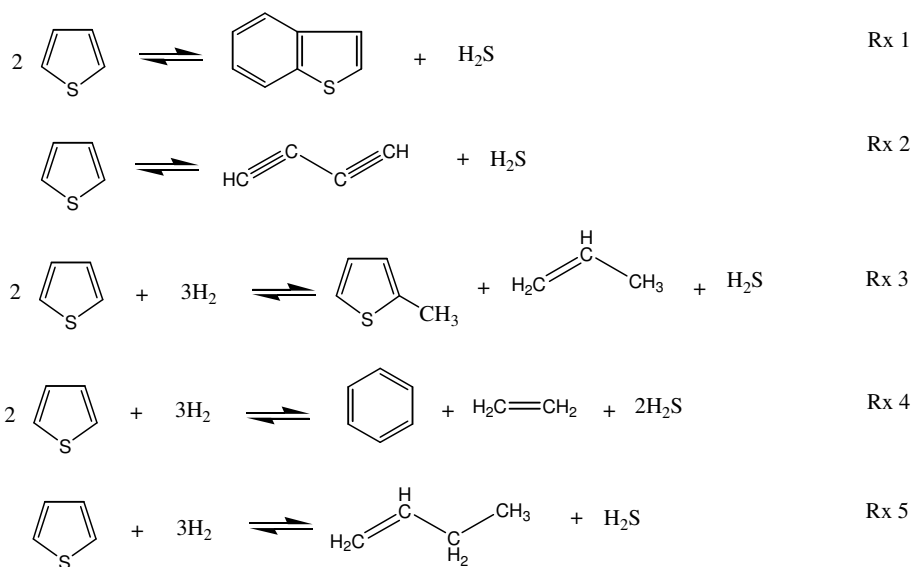

Figure 35. Set of thiophene over zeolites reactions evaluated thermodynamically.

The commercial process simulator software Hysys was used to aid in the equilibrium constant calculations of the set of simultaneous reactions detailed above. Calculations were developed using same operation conditions as reported in experimental studies described in section 6: temperatures between 623 K and 723 K, pressure 200 kPa, thiophene concentration of 5 wt% in the thiophene/n-octane mixture, and an arbitrary total incoming flow of 1000 kgmol/h. For the simulation case in presence of hydrogen an excess flow of 10 kgmol/h was added. The fluid property package used was the Peng Robinson Soave (PRSV) equation of state, which was considered the best alternative to model the thermodynamic behavior of the compounds present in the reaction set.

The Hysys option used to determine the reaction equilibrium constants was "equilibrium reactor unit" that represents an algorithm for solving simultaneously the set of reactions at equilibrium. The chemical equilibrium constants calculated are given in Table 5 and the equilibrium compositions and conversions of thiophene in presence and absence of hydrogen are reported in Tables 6 and 7, respectively.

Table 5. Equilibrium constants for thiophene cracking over ZSM5 zeolite, 350-450°C temperature range, 10 wt% thiophene in thiophene/n-octane mixture, 200 kPa (refer Figure 35).

T [°C]	350°C	400°C	450 °C
K Rx 1	2.949×10^{10}	2.54×10^{10}	2.401×10^{10}
K Rx 2	5.21×10^{-19}	7.604×10^{-17}	5.75×10^{-15}
K Rx 3	1.557×10^{4}	1.700×10^{3}	2.518×10^{2}
K Rx 4	1.877×10^{9}	2.602×10^{8}	4.862×10^{7}
K Rx 5	3.444×10^{3}	3.869×10^{2}	59.05

Regarding the reactions involved under presence of hydrogen, thiophene conversion is represented for competitive reactions from 1 to 5 (see Figure 35). Observing the equilibrium constants calculated it can be noticed that for the temperature range studied, the equilibrium constants for reactions 1 and 4 are consistently much higher than the equilibrium constants for reactions 2, 3 and 5; indeed so high values indicate that reaction 1 and 4 are almost irreversible. As a result, in presence of hydrogen and under conditions evaluated, the thermodynamic favored products from thiophene conversion are benzothiophene and H_2S (reaction 1) as well as, benzene, ethene and H_2S (reaction 4).

On the other hand, in all of the cases in presence of hydrogen, the estimated equilibrium conversion of thiophene for reactions 2, 3 and 5 were zero, indicating that these reactions are equilibrium limited under studied conditions, thus the production of butadiyne (reaction 2), methyl-thiophene (reaction 3), and butene (reaction 5) from thiophene conversion, as proposed by Welters *et al.* (1994),

Saintigny *et al.* (1999), Shan *et al.* (2002) and Yu *et al.* (1999), seems to be unlikely to happen. Furthermore, the higher conversion of the reaction 1 ($\approx$99.5%) in front of the conversion of reaction 4 ($\approx$0.5%) indicate that the conversion of thiophene is more selective to the production of benzothiophene than benzene.

Table 6. Equilibrium composition and conversion for thiophene cracking over ZSM5 zeolite in presence of H_2, 350-450°C temperature range, 10 wt% thiophene in thiophene/n-octane mixture, 200 kPa.

Components	T 350 °C wt%	T 400 °C Wt%	T 450 °C wt%
H_2	0.02	0.02	0.02
H_2S	2.03	2.03	2.03
Ethene	0.01	0.00	0.00
Propene	0.00	0.00	0.00
Butenes	0.00	0.00	0.00
Butadiyne	0.00	0.00	0.00
Benzene	0.02	0.01	0.00
Thiophene	0.00	0.00	0.00
Methyl-Thiophene	0.00	0.00	0.00
Benzothiophene	7.94	7.96	7.97
n-Octane	89.98	89.98	89.98
Thiophene Conversion, %			
Rx1	99.53	99.79	99.91
Rx2	0	0	0
Rx3	0	0	0
Rx4	0.47	0.21	0.09
Rx5	0	0	0

On the topic of the thiophene conversion in absence of hydrogen, only reactions 1 and 2 are competitive, being reaction 1 the thermodynamically favored, hence benzothiophene seems to be the only product from the cracking of thiophene in absence of hydrogen.

Table 7. Equilibrium composition and conversion for thiophene cracking over ZSM5 zeolite in absence of H_2, 350-450°C temperature range, 10 wt% thiophene in thiophene/n-octane mixture, 200 kPa.

Components	T 350 °C wt%	T 400 °C Wt%	T 450 °C wt%
H_2	0.00	0.00	0.00
H_2S	2.03	2.03	2.03
Ethene	0.00	0.00	0.00
Propene	0.00	0.00	0.00
Butenes	0.00	0.00	0.00
Butadiyne	0.00	0.00	0.00
Benzene	0.00	0.00	0.00
Thiophene	0.00	0.00	0.00
Methyl-Thiophene	0.00	0.00	0.00
Benzothiophene	7.97	7.97	7.97
n-Octane	90.00	90.00	90.00
Thiophene Conversion, %			
Rx1	100	100	100
Rx2	0	0	0

Consequently, the thermodynamic analysis is valuable to demonstrate that the thiophene conversion over zeolites, in presence or absence of hydrogen, or even in the case of the use of co-reactants (case of n-octane), likely produce heavier thio-aromatics, as benzothiophene, that can condensate ending in coke over the catalyst, as is shown in Figure 5.

10. GASOLINE DESULFURIZATION OVER ZEOLITES IN FIXED BED UNITS

Most of the experimental studies that support the use of zeolites as adsorbent and cracking catalyst of sulfur compounds have been carried out in fixed bed reactors.

10.1. General description of the swing fixed bed unit operation

Separating fixed bed reactors employing adsorption can utilize abrupt pressure or temperature changes for regeneration. The swing reactors, either pressure swing (PSR) and temperature swing (TSR), are drawn from adsorption systems: pressure and temperature swing adsorbers. Both classes of separating reactors are basically cyclic in operation. Extending the application of swing adsorption technology to reactions systems appears to be straightforward if swing reactors can improve

yields or selectivity or can decrease capital or operating costs when both reaction and separation are necessary. Takashi and Peter (2005) preset an extensive review of recent publications on swing reactions systems.

```
                    ┌─────────────────┐
                    │  Fresh Catalyst │
                    └─────────────────┘
                             │
              Treatment at 773 K in O₂ 1h and
                    Cool in He Flow
                             │
                             ▼
                    ┌─────────────────┐
          ┌────────►│ Catalyst at 363 K│
          │         └─────────────────┘
          │                  │
          │          Thiophene Adsorption
          │                  │
          │                  ▼
          │    ┌──────────────────────────┐
          │    │ Catalyst + Adsorbed Thiophene│
          │    └──────────────────────────┘
          │                  │
          │      Flush with He to Remove Weakly
          │        Bound Thiophene (15 min)
          │                  │
    Cool in He Flow          ▼
          │    ┌──────────────────────────┐
          │    │  Catalyst +  Adsorbed Thiophene │
          │    │       after Cleaning      │
          │    └──────────────────────────┘
          │                  │
          │      Regeneration (He, H₂, C₃H₈ or O₂)
          │           (773 K or 873 K)
          │                  │
          │                  ▼
          │         ┌─────────────────┐
          └─────────│ Regenerated Catalyst │
                    └─────────────────┘
```
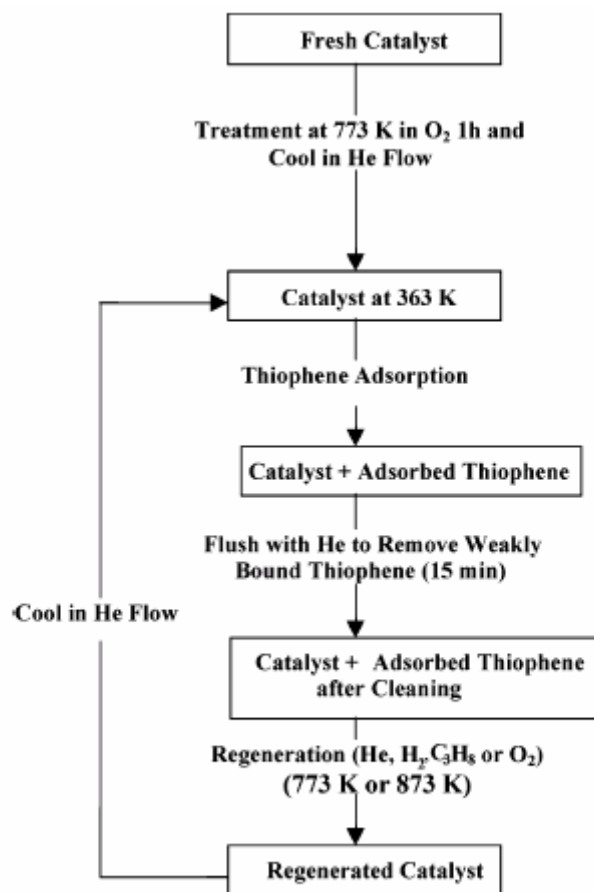
 ᵃ TPH, thiophene.

Figure 36. Thiophene Adsorption-Desorption Cycles Carried out on H-ZSM5 Zeolite (Si/Al = 13) (Reprinted with permission from Langmuir, vol. 20, Chica *et al.*, "Adsorption, Desorption and Conversion of Thiophene on H-ZSM5", p. 10982-10991, Copyright 2004 American Chemical Society)

The application of a temperature swing reactor in new gasoline desulfurization processes over zeolites can be considered due the role play by the zeolite as a catalyst-adsorbent material. The fixed bed reactor used by Chica *et al.* (2004), during their studies of thiophene conversion over zeolites, could be considered as a temperature swing reactor. The adsorption-desorption protocols

are described in Figure 36. Fresh zeolite adsorbents were treated in flowing dry air at 773 K for 1 h. Adsorption measurements were carried out at 363 K using liquid thiophene introduced into a flowing He-Ar stream. Thiophene was vaporized immediately upon injection at 423 K and transferred into the reactor. Typically, thiophene was initially depleted from inlet streams for a period of time, after which its concentration increased and ultimately reached inlet levels, as each adsorbent reached saturation coverage. Adsorbed amounts were measured from a time integral of the differences between inlet and outlet concentrations. After saturation, samples were treated under He flow at 363 K for 0.25 h to remove weakly adsorbed thiophene before starting regeneration protocols. The removal of adsorbed species via desorption or reaction was examined using four gas streams (O_2, He, H_2 and C_3H_8) at 773 and 873 K for 1 h. The effluent stream was analyzed continuously during desorption-reaction protocols with on-line mass spectrometry and gas chromatography.

11. GASOLINE DESULFURIZATION OVER ZEOLITES IN FLUIDIZED CIRCULATING BED REACTORS

Problems of fluid distribution, mass transfer limitations, low overall conversion, and adsorption of reaction products leading to reduce gasoline quality and coke formation are all disadvantages of fixed bed systems when used for catalytic desulfurization.

Taking into consideration the reaction mechanism of thiophene over zeolites described in section 6, the gasoline desulfurization over zeolites could be a process with significant levels of coke formation. Thus a twin fluid-bed reactor and regenerator bed system seems to be a good approach for a new gasoline desulfurization process where it is necessary to maintain catalyst activity in a continuous operation. A discussion of few works reported in this area is done in this section.

An experimental study of sulfur hydrocarbons conversion over zeolites using a fluidized bed reactor was developed by Collins *et al.* (1995, 1996). The catalyst used contained 25 wt% of H-ZSM5 zeolite with a Si/Al molar ratio of 25. The reaction conditions were: 643 – 723 K, 50 – 250 psig, and 0.1 – 2 h^{-1} WHSV. The sulfur in organic compounds was converted to H_2S. The authors claim that the process could be used to desulfurize either light gases or gasoline streams with light olefins being upgraded to more valuable gasoline range materials. They reported that up to 61% of the sulfur in the feed was converted to H_2S. These studies showed the H-ZSM5 catalytic ability to remove sulfur compounds without hydrogen addition.

Another experimental work with a fluidize bed reactor was reported by de Lasa *et al.* (2006), they evaluated the hydrodesulfidation reactions of ethyl

mercaptan (EM) dissolved in n-octane (nC8) on H-ZSM5 catalyst (20 wt% ZSM-5) without hydrogen addition and using a mini-fluidized bed CREC riser simulator reactor (de Lasa, 1992). These researchers reported a maximum EM conversion of 50.85% and nC_8 conversion of 22.87% at 450 °C, 60s, C/O=2.5, for concentration of 10 wt% of EM in nC_8 (Figures 37 and 38).
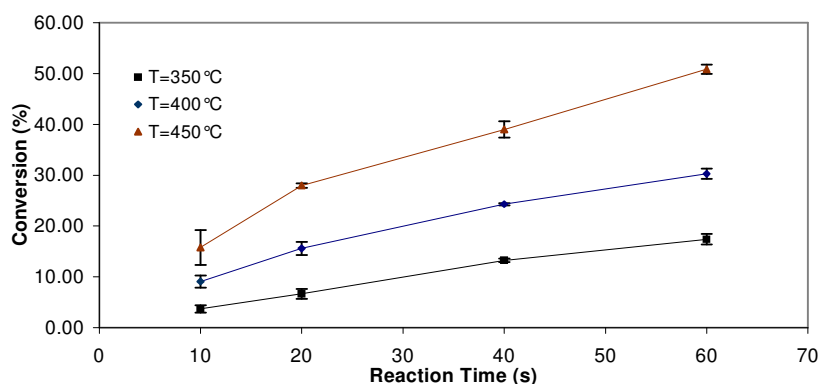

Figure 37. Conversions of ethyl mercaptan versus time. Reaction conditions: T=350°C, 400°C and 450°C, C/O=2.5. Feed composition: 10wt.% EM/nC_8. Error bars correspond to standard deviation (Reprinted with permission from Ind. Eng. Chem. Res., vol. 45, de Lasa *et al.*, "Catalytic Desulfurization of Gasoline via Dehydrosulfidation", p. 1291-1299, Copyright 2006 American Chemical Society)

Figure 38. Conversions of nC_8 versus time. Reaction conditions: T=350°C, 400°C and 450°C, C/O=2.5. Feed composition: 10wt.% EM/nC_8. Error bars correspond to standard deviation (Reprinted with permission from Ind. Eng. Chem. Res., vol. 45, de Lasa *et al.*, "Catalytic Desulfurization of Gasoline via Dehydrosulfidation", p. 1291-1299, Copyright 2006 American Chemical Society)
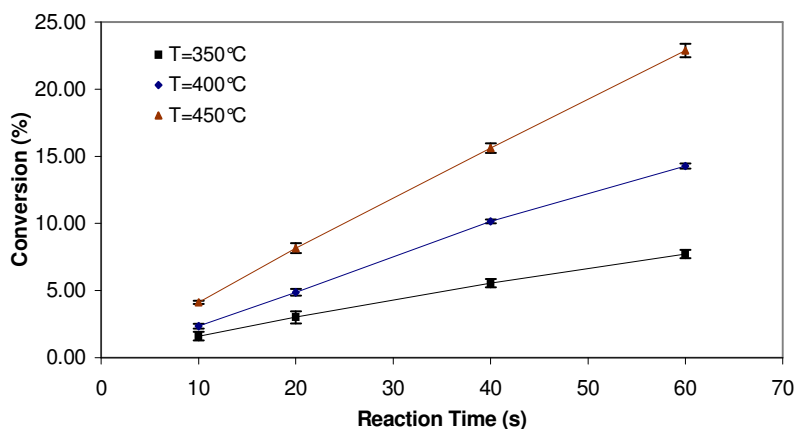
Taking into consideration these results, de Lasa *et al.* (2006) suggested that there is a strong competition for the acid sites of the ZSM-5 catalyst promoting both, de-hydrosulfidation and catalytic cracking. It appears that given the significant differences in gas phase concentrations between nC_8 and EM, between 10 to 20 times, there should be either a bigger adsorption affinity of EM versus nC_8 or alternatively a much faster intrinsic rate of EM de-hydrosulfidation versus the one for the nC_8 cracking rate.

With respect to the product distribution, the results obtained by de Lasa *et al.* (2006) show that catalytic runs with a mixture of EM and nC_8 were richer in trans-butene compared with pure nC_8 runs. This indicates that EM conversion promotes the formation of trans-butene via inter-molecular de-hydrosulfidation reaction (refer to equations 2 and 3, Section 6). Furthermore, the amounts of ethene were also higher for the catalytic runs using mixtures of EM and nC_8 versus the ones using pure nC_8. This also was considered a good indication of formation of ethene via intra-molecular de-hydrosulfidation reaction (refer to equation 1, Section 6).

A similar sulfur removal efficiency than showed by de Lasa *et al.* (2006) has been claimed by Bai *et al.* (2004), in the commercial process so-called "the subsidiary riser technology for olefin reduction in FCC naphtha". This subsidiary riser technology for olefin reduction in FCC naphtha used a reaction-regeneration process configuration as suggested in the present review. Bai *et al.* (2004) reported an olefin reduction in the cracked naphtha from 55 to 35 vol%, with minimum octane loss by significant increment of the aromatics content (until 50%), and a sulfur removal efficiency of 50%. However, the applicability of this process must be carefully considered when high aromatics content in gasoline is undesirable.

11.1. General description of the twin bed operation

The CREC "Riser Simulator" mimics the operating conditions of an industrial unit in riser reactor in terms of reaction time, temperature, hydrocarbon partial pressures and catalyst/oil ratios, allowing the testing and development of new catalysts.

The CREC riser simulator is a bench scale mini-fluidized bed unit with a 50 cm^3 capacity, allowing the loading of 1 gr. of catalyst. A schematic diagram of a CREC Riser Simulator is reported in Figure 39 (de Lasa, 1992). An impeller located in the upper section and a basket containing the catalyst placed in the central section, are the main components. Upon rotation of the impeller, gas is forced downwards in the outer reactor annulus. This creates a lower pressure in the central region of the impeller with a spiraling upwards flow of gas in the catalyst chamber. Two porous plates grids keep the catalyst inside the central

chamber under high fluidization conditions. The CREC riser simulator is equipped with auxiliary components allowing instantaneous feeding and quick removal of reaction products. The Figure 40 shows a schematic description of the CREC riser simulator and associated valves and accessories.
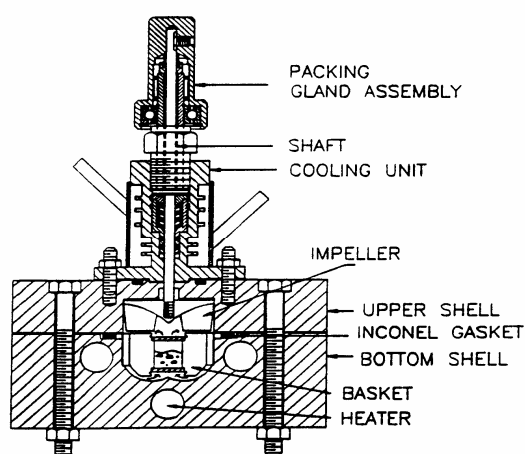
Figure 39. Schematic description of the CREC riser simulator (de Lasa, 1992).

The CREC riser simulator provides key data for riser and downer units modeling:
a) Intrinsic kinetic parameters of complex reactions.
b) Adsorption constants and effective diffusivities, allowing the development of phenomenologically based heterogeneous kinetic models.
c) Reaction enthalpies needed for the overall enthalpy balances.

Applications of the CREC Riser Simulator to catalytic cracking have been widely reported, excellent examples are the studies conducted at CREC on FCC catalysts (Atias *et al.*, 2003) and the evaluation of zeolites as desulfurization catalyst (de Lasa *et al.*, 2006).

Figure 40. Schematic description of CREC riser simulator and associated valves and accessories

11.2. Kinetic modeling and parameter estimation

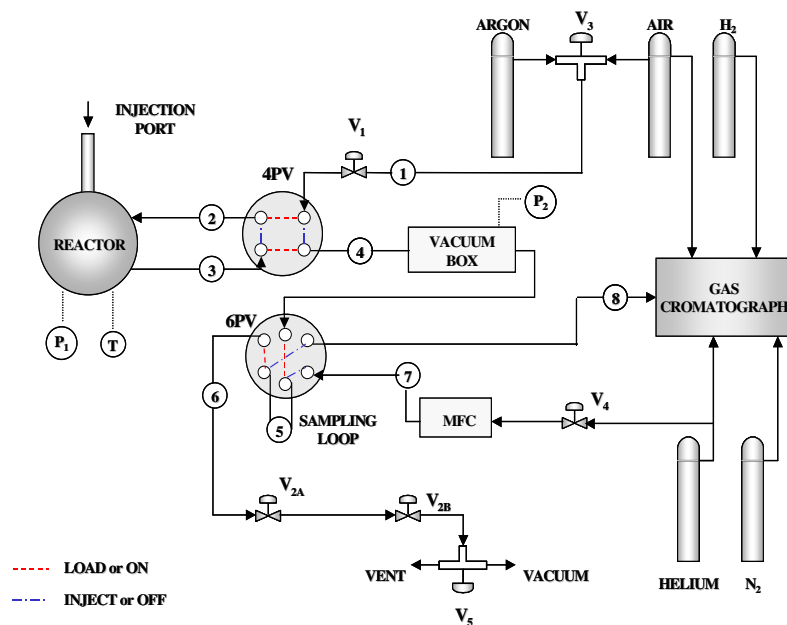de Lasa *et al.* (2006) proposed that the total rate of consumption of EM can be viewed as the addition of the intra-molecular and inter-molecular de-hydrosulfidation reaction rates (refer to Section 6). Regarding the intra-molecular de-hydrosulfidation reaction, it is assumed to be of first order, a chemical reaction involving a single species. On the other hand, the inter-molecular de-hydrosulfidation reaction was considered second order given it is the result of the interaction of two sulfur-containing molecules. This view of de-hydrosulfidation is represented as:

$$- r_{EM} = k_1 C_{EM} + k_2 C_{EM}^2 \tag{4}$$

where r_{EM} represents the rate of EM consumption in moles gcat^{-1} s^{-1}, C_{EM} the EM concentration in moles cm^{-3} and k_1 and k_2 the kinetic constants for intra-molecular and inter-molecular de-hydrosulfidation respectively.

Also, the inter-molecular de-hydrosulfidation reaction is considered first order, with inter-molecular de-hydrosulfidation being non-elementary. Under these conditions the overall reaction rate becomes:

$$-r_{EM} = k_1 C_{EM} + k_2 C_{EM} = k C_{EM} \tag{5}$$

Regarding equations 4 and 5, they only contain catalytic de-hydrosulfidation effects, thermal reactions were neglected on the basis of experimental results obtained by de Lasa *et al.* (2006).

Equations (4) and (5) were solved in the context of the CREC riser simulator species balances in conjunction with a quasi-steady state assumption:

$$\frac{dC_{EM}}{dt} = r_{EM} \frac{W_c}{V_r} \tag{6}$$

where W_c is the catalyst weight in gcat and V_r is the reactor volume in cm^3

Substituting equation 5 into equation 6 gave:

$$\frac{dC_{EM}}{dt} = -k C_{EM} \frac{W_c}{V_r} \tag{7}$$

Equation 7 was integrated and the fractional EM conversion, X_{EM}, was expressed in terms of both kinetic and operational parameters:

$$-\ln(1 - X_{EM}) = \frac{k W_c}{V_r} t \tag{8}$$

Hence linear regression of equation 10 in a semi-logarithmic plot gave (kW_c/V_r). Considering W_c and V_r, were known, k parameter were calculated. Table 8 reports the obtained k at different temperatures with their 95% confidence limits (de Lasa *et al.*, 2006).

Table 8. Values of kinetic constant at 623, 673 and 723 K (de Lasa *et al.*, 2006).

Temperature (K)	k (cm^3/gcat.s)	±C.L. (95%)	R^2
623	1.11	0.0424	0.9624
673	2.05	0.1169	0.8574
723	3.88	0.1956	0.9184

In order to obtain both activation energy and pre-exponential factor, the Arrhenius equation was modified via re-parameterization and this to reduce cross-correlation between parameters. With this end a central average temperature (T_{av}) was defined as follows,

$$k = k_o' \, exp[-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_{av}})] \tag{9}$$

with E being the activation energy, k_o' a pre-exponential factor, R the ideal gas constant, T and T_{av} the reaction and average temperatures respectively.

Using equation (9), both the activation energy and pre-exponential factor were calculated via linear regression in a ln (k) versus ($1/T-1/T_{av}$) plot. The following values were thus obtained:

E= 46.79 $\pm$ 32.76 kJ/mole

k_o' = 9112.48 $\pm$ 359.72 (cm^3/gcat.s)

However, and in order to have better estimate of these parameters, a regression was performed using the following expression:

$$X_{EM} = 1 - exp\left[-\frac{W_c}{V_r}t\left(k_o' \, exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{av}}\right)\right)\right)\right] \tag{10}$$

Equation 10 is a non-linear relation in terms of k_o' and E parameters. This equation was fitted using a non-linear regression algorithm and the above quoted kinetic parameters, E= 46.79 KJ mole^{-1} and k_o' = 9112.48 cm^3 gcat^{-1}.s^{-1}, were used as initial guesses. The following were the resulting k_o' and E values, with these parameters being reported with their 95% confidence intervals:

E = 46.66 $\pm$ 34.84 kJ/mole

k_o' = 9195.83 $\pm$ 218.75 (cm^3/gcat.s)

Using these constants, the calculated EM conversions (equation 10) was compared by de Lasa *et al.* (2006) with their experimental data. Figure 41 reports a reasonable random distribution of residuals with a 5.16% linear regression line difference with respect to the 45 degrees perfect agreement case.
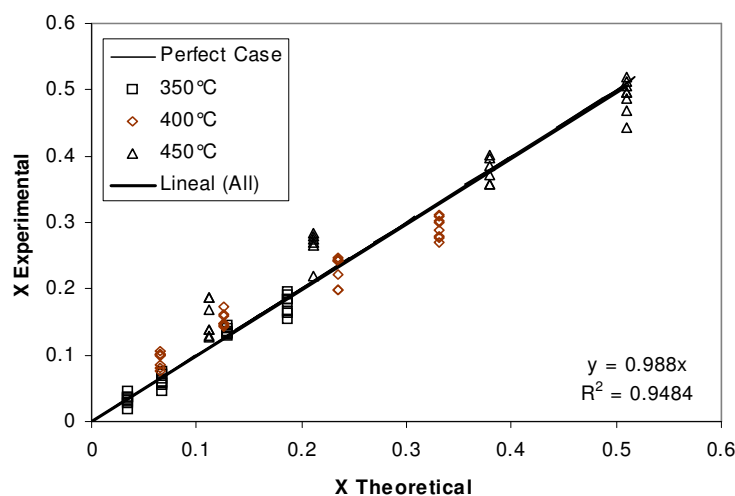
Figure 41. Fractional experimental conversion versus Fractional theoretical conversion (Reprinted with permission from Ind. Eng. Chem. Res., vol. 45, de Lasa *et al.*, "Catalytic Desulfurization of Gasoline via Dehydrosulfidation", p. 1291-1299, Copyright 2006 American Chemical Society)

In view of these results, de Lasa *et al.* (2006) concluded that the assumption of a first order law provides overall a good approximation for the EM conversion. There was however some deviation of the first order law at the higher temperatures and this was assigned to the contribution of two factors: a) increased influence of the intermolecular conversion of EM, a potentially second order reaction, and b) potential shift in the reaction order for the intermolecular conversion, from first to second as temperature increases.

In spite of this, the dominant first reaction order for the EM conversion was an encouraging finding. It allows them to speculate that catalytic de-hydrosulfidation will be as effective at lower mercaptans concentrations. They appointed that this observation was consistent with equation (10), where mercaptan conversion is independent of the mercaptan initial concentration.

This study is a preliminary approach to expand the idea to the real composition of a gasoline and the application of the ZSM5 to a mixture of sulfur compounds/hydrocarbons (real or synthetic). The needed following paths are under development in the CREC, considering all the previous work in this field (Yu *et al.* 1999 and 2003, Li *et al.* 2001, Chica *et al.* 2004, de Lasa *et al.* 2006, Collins *et al.* 1995 and 1996).

12. CONCLUSIONS AND PERSPECTIVES

The following are the most relevant conclusions and perspectives of this review:

a) New environmental fuel regulations mandate that the average sulfur content of gasoline must be lowered to 30 ppm. Considering that FCC gasoline represents almost 40% of the total gasoline pool and it is the major sulfur contributor, up to 85–95%, the reduction of sulfur impurities in this stream has become an important issue. In this sense, most refiners have adopted the post-treating FCC gasoline as the more viable and less costly path for meeting sulfur environmental regulations.

b) Conventional hydrotreating of FCC gasoline decreases its quality by octane number loss. Moreover, the use of hydrogen adds important costs, reasons why the latest gasoline desulfurization studies are orientated to desulfurization processes free of hydrogen. There are new desulfurization processes that support the use of zeolites as selective sulfur adsorbent and cracking catalysts, being the ZSM5, belonging to the pentasil family, the zeolite that shows the better adsorption selectivity.

c) More fundamental work is still needed to elucidate the chemical reaction mechanisms and the special role assigned to the adsorbed intermediates species involved in the process of adsorption and cracking of sulfur compounds on zeolites. The possibility of different transition states in the reaction of sulfur compounds on zeolites, mainly thiophene and derivatives, should be addressed more deeply with both theoretical and experimental studies. These different transition states (alkoxide, carbocation or zwitterion) and the relative extent of each step on certain zeolite with controlled shape and size, condition the resulting transition structures. In this respect, diverse local acidity and basicity may affect differently the stabilization of one structure versus another. Also the H-donor co-feeding can play an important role.

d) An in-depth understanding of the relative contribution of each transition state on a given zeolite would help to design a tailor made catalysts for reactions such as: desulfurization, cracking or oligomerization, considering ionic substitution or inorganic chemical modification. Molecular modeling of the transition state structures and the analysis of the local electric field of the zeolites around the active sites on each surface would bring more light on these mechanistic aspects.

e) New desulfurization processes with zeolites as catalyst can be implemented in fixed and fluid bed reactors. The application of a temperature swing fixed bed reactor in gasoline desulfurization over zeolites is based on the role played by the zeolite as a catalyst-adsorbent material. Gasoline desulfurization over zeolites could be a process with significant levels of coke formation. Thus, a twin fluid-bed reactor and regenerator bed system can be the best approach for a new gasoline desulfurization process where one can maintain catalyst activity in a continuous operation.

NOTATION

C_{EM}	EM concentration (mole/cm^3)
E	activation energy (J/mole)
k	kinetic constant (cm^3/gcat.s)
k_o	pre-exponential factor
$k_o^{'}$	pre-exponential factor after reparametrization
k_1	kinetic constant for the intra-molecular (cm^3/gcat.s).
k_2	kinetic constant for the inter-molecular de-hydrosulfidation (cm^3/gcat.s).
K_1	equilibrium constant equation (1)
K_2	equilibrium constant equation (2)
K_3	equilibrium constant equation (3)
$K\,Rx1$	equilibrium constant reaction 1
$K\,Rx2$	equilibrium constant reaction 2
$K\,Rx3$	equilibrium constant reaction 3
$K\,Rx4$	equilibrium constant reaction 4
$K\,Rx5$	equilibrium constant reaction 5
r_{EM}	reaction rate of EM (mole/gcat.s).
R	ideal gas constant (8.314 J/mole.K)
t	reaction time (s)
T, T_{av}	temperature and average temperature respectively (K)
V_r	reactor volume (cm^3)
W_c	catalyst weight (g)
X_{EM}	fractional conversion of EM
ΔG	Gibbs energy change
ΔH	enthalpy change

Abbreviations

BA	Brönsted acid
$C_2^{=}$	ethene
CHA	chabazite
CREC	chemical reaction engineering center
CTO, C/O	catalyst oil ratio
DFT	density functional theory
DiE-S	diethyl sulfide
EFAL	extraframe aluminium
EM	ethyl mercaptan
FAU	faujasite
FCC	fluid catalytic cracking
FER	ferrierite

FTIR	Fourier transformed infra red
GC	gas chromatography
HCO	heavy cycle oil
HDS	hydrodesulfurization
IR	infra red
LA	Lewis acid
LB	Lewis basic
LCO	light cycle oil
LPG	liquid petroleum gas
LTL	linde type L
MFI	ZSM-5 (**Z**eolite **S**ocony **M**obil - five /Silicalite-1) structure
MOR	mordenite
MS	mass spectrometry
MWW	SSZ-25 (**S**tandard Oil **S**ynthetic **Z**eolite) structure
nC_8	n-octane
NMR	nuclear magnetic resonance
PM3	parameterized method 3
PSR	pressure swing adsorption
$tC_4^=$	trans butene
TPD	temperature programmed desorption
TSR	temperature swing adsorption

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