



**ON THE INTERACTION OF THIOPHENE AND ZEOLITE-Y IN THE
THIOPHENE-BASED OLIGOMERS FORMATION**

**SOBRE LA INTERACCIÓN ENTRE TIOFENO Y ZEOLITA-Y EN LA FORMACIÓN
DE OLIGOTIOFENO**

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Abstract

Due to the inconsistencies in the literature about the structure of thiophene oligomers, formed by the interaction between thiophene and the Brönsted acid sites of zeolite Y, the direct analysis of these oligomeric species is fundamental, mainly to understand how they are made up and their correct structure. The materials used were zeolite Y in its protonic (HY) and sodic (NaY) form. The interaction between thiophene and the zeolitic material was performed by the adsorption of thiophene at room temperature using a solution of thiophene in *n*-octane (100-700 ppmw), leading to the formation of cationic thiophene oligomers that are trapped inside the cavities of HY, among other non-oligomeric species. The thiophene-zeolite Y interaction occurs through the Brönsted acid sites by two possible routes: i) by electrophilic attack to the pair of free electrons in sulfur, forming oligothiophene whose size is limited by the structure of zeolite and, ii) by interaction with the α -carbon that leads to the formation of H₂S, thiols and hydrocarbons with carbons with sp³ hybridization.

Keywords: Thiophene, zeolite Y, Brönsted acid sites, oligomers.

Resumen

Debido a las inconsistencias en la literatura sobre la estructura de los oligómeros de tiofeno, formados por la interacción entre tiofeno y los sitios ácidos de Brönsted de la zeolita Y, el análisis directo de dichas especies oligoméricas es fundamental, principalmente para entender cómo se forman y definir su estructura correcta. Los materiales empleados fueron zeolita Y en su forma protónica (HY) y sódica (NaY). La interacción entre tiofeno y el material zeolítico se hizo mediante la adsorción de tiofeno a temperatura ambiente empleando una solución de tiofeno en *n*-octano (100-700 ppmw), llevando a la formación de oligómeros catiónicos de tiofeno que quedan atrapados dentro de las cavidades de la HY, entre otras especies no oligoméricas. La interacción tiofeno-zeolita Y se da a través de los sitios ácidos de Brönsted por dos posibles vías: i) por ataque al par de electrones libres del azufre formando oligotiofeno cuyo tamaño está limitado por la estructura de la zeolita y, ii) por interacción con el carbono α que conduce a la formación de H₂S, tioles e hidrocarburos con carbonos con hibridación sp³.

Palabras clave: Tiofeno, zeolita Y, sitio ácido de Brönsted, oligómeros.

1 Introduction

Semiconductor materials are subject of scientific interest because at present, their properties allow them to be applied in the electronic industry, where they

are commonly found as compounds based on silicon or gallium; however, at the end of 1970s, some π -conjugated bond polymers with similar properties to inorganic semiconductors were studied, among the most important, the ability to conduct electricity (Shirakawa *et al.*, 1977).

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These materials, generally called organic semiconductors or synthetic metals (Otterstedt *et al.*, 1986), represent an interesting alternative in high-impact technological applications, such as organic light-emitting diodes or organic field-effect transistors (OLEDs and OFETs, respectively), sensors, low cost integrated circuits and sensitized solar cells (DSSC) (Brütting, 2006; Coropceanu *et al.*, 2007). Therefore, organic materials with conductive capacity have been widely studied in different areas, mainly academic and industrial (Brütting, 2006); nevertheless, a lot of studies are also required to evaluate their efficiency in use and conversion of energy, because until now, inorganic semiconductors are still the most used.

Among the organic semiconductors with the greatest number of applications, are the thiophene oligomers (Mishra *et al.*, 2009), chemical species that have a resonant structure and, consequently, exhibit electronic delocalization (Schulz *et al.*, 1999a; 1999b; Cerqueira *et al.*, 2008). Thiophene oligomers that are not coupled with other compounds are known as α -oligothiophenes (α -nT) or β -oligothiophenes (β -nT), depending if the α or β carbon is the binding element, where α -nT have greater applications compared to β -nT due to their low conjugation (Becker *et al.*, 1996; Bäuerle, 2008). But, in some cases, the α -nT are more efficient (in OFETs) than the coupled polythiophenes or some compounds based on amorphous silicium (Bäuerle, 2008).

Therefore, in recent years, the study of the electronic properties of thiophene oligomers and the synthesis methods to obtain them, is relevant. Highlighting the synthesis methods through polycondensation, dehalogenation and polymerization reactions, to form both, α -nT and functionalized oligothiophenes (Mishra *et al.*, 2009). On the other hand, it has been reported about the formation of thiophene oligomers into the spaces confined to zeolitic materials; by the interaction of the monomer with the various materials; process that requires a more complex analysis, since the proposals on the structure of the π -conjugated materials differ between the different authors. In this sense, Caspar *et al.* (1991) reported the formation of α -nT species and functionalized oligothiophenes by the interaction of the monomer with ZSM-5. Later, Geobaldo *et al.* (1999) concludes that the interaction of thiophene with protonic zeolite-Y occurs through the Brønsted acid sites of zeolite, forming cationic thiophene oligomers, dithiophene and trithiophene, which differ from the species proposed by Caspar and colleagues. Futhermore, Yang *et al.* (Hernández-Maldonado *et*

al., 2004; Hernández-Maldonado & Yang, 2004; Takahashi *et al.*, 2002; Yang *et al.*, 2001) developed materials of the Cu(I)-Y and Ag-Y type, in which they propose that copper and silver interact with the π -bonds of molecule to form undefined π -conjugated complexes. It is noteworthy that, only Geobaldo *et al.* (1999) and Caspar *et al.* (1991) directly analyzed the species formed in the cavities of the zeolitic material in its protonic form, so that, recent studies have realized corrected structural proposals of oligothiophenes made up by the interaction with the different zeolitic materials (Whiting *et al.*, 2014; Valencia *et al.*, 2016). Due to the structural inconsistencies of thiophene oligomers reported in the studies mentioned above, a detailed analysis of these is necessary. Therefore, in this work, the species are analyzed directly through spectroscopic techniques (FT-IR, UV-Vis and NMR) altogheter with the proposal of reaction routes. The results obtained in this study show that the interaction between protonic zeolite-Y and thiophene monomer can occur in two ways: one, which forms H₂S, thiols, and hydrocarbons with carbons with sp^3 hybridization; and a second one, which forms the cationic α -nT within the cavities of protonic zeolite, from which a proposal of the correct structures of the thiophene oligomers is made.

2 Materials and methods

2.1 Reactives

Ammonium zeolite-Y (UOP Y-84, molecular sieves Si/Al=1.6) was calcined, at 450 °C for 24 hours in a programmable temperature oven (Advantec KM-280 Electric Muffle Furnaces 393) in static air at atmospheric pressure to obtain zeolite-Y in a protonic form (HY sample). Zeolite-Y was also used in a sodic form; obtained by three ion exchanges with a 0.01 M NaNO₃ solution; HY was leave in constant stirring with the NaNO₃ solution (0.01M) for 24 hours, the obtained product was filtered and washed with twice the volume of deionized water (NaY sample). All materials obtained were thermally activated at 450 °C for 24 hours in a programmable temperature oven (Advantec KM-280 Electric Muffle Furnaces 393) in static air at atmospheric pressure. Upon completion of activation, solids were cooled at room temperature before use.

2.2 Characterization

The materials were vacuum to 30 °C at a pressure of 10^{-3} Pa in a Cole-Parmer® vacuum furnace (StableTemp™) of 19.8 L. Immediately, an infrared spectroscopy was used at room temperature in the diffuse reflectance mode (Bruker IFS 66 FTIR) with a resolution of 2 cm^{-1} . The ultraviolet-visible analysis of the undiluted samples was measured by diffuse reflectance in a UV-Vis spectrometer (Varian Cary 5) with a resolution of 0.5 nm. In addition, solid-state ^{13}C Nuclear Magnetic Resonance spectroscopy was used (model ASX-300, Bruker) of 300 MHz. Spectra were obtained at 75.47 MHz with a Probe 4 mm, 31P-15N, rotation speed 5 KHz, contact pulse 1 ms and a repetition time of 6 s, by the CP-MAS technique.

2.3 Adsorption

Test solution was prepared with thiophene (99% Aldrich) dissolved in *n*-octane (99%, JT Baker), total sulfur concentration varied with increments of 100 ppmw (100 to 700). The experiments were carried out by adsorption in equilibrium at room temperature with the test solution, by adding the HY and NaY samples, respectively, inside 25 mL Erlenmeyer flasks hermetically sealed and left it in constant stirring during adsorption. Each sample was identified by the code of adsorbent and the initial amount in parts per million of sulfur in the solution.

3 Results and discussion

3.1 Acid sites and adsorption (IR)

Figures 1 and 2 show the IR spectra corresponding to HY and NaY, respectively. After the adsorption process, bands corresponding to the Brönsted acid sites of zeolite HY (acidic Brönsted sites in the supercavity, $\sim 3652\text{ cm}^{-1}$, and in the sodalite cavity, $\sim 3554\text{ cm}^{-1}$) decrease considerably (Breck, 1974; Uytterhoeven *et al.*, 1965; Uytterhoeven *et al.*, 1968). In the case of NaY, only small bands around 3648 cm^{-1} and 3547 cm^{-1} were observed, belonging to the Brönsted acid sites mentioned above. These bands appear in the NaY sample due to the obtention procedure, since it is known that ion exchange does not occur at 100% in zeolites (Breck, 1974), with a fraction of Brönsted acid sites remaining in NaY zeolite.

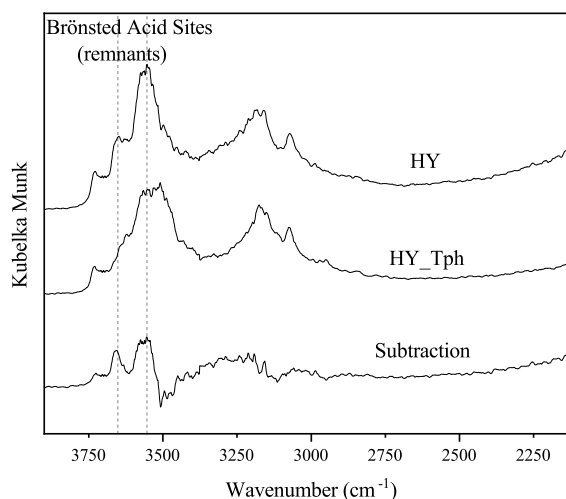


Fig. 1. IR spectra: Protonic Zeolite-Y (HY), Protonic Zeolite-Y after adsorption of thiophene (HY_Tph) and subtraction of these two spectra.

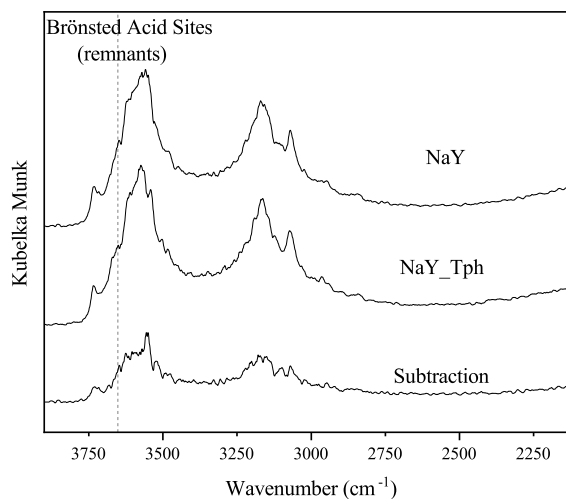


Fig. 2. IR spectra: Sodic Zeolite-Y (NaY), Sodic Zeolite-Y after adsorption of thiophene (NaY_Tph) and subtraction of these two spectra.

The band that remains constant in the OH region ($\sim 3730\text{ cm}^{-1}$) corresponds to terminal silanol groups formed by structural defects. These are very weak acid centers and do not interact with thiophene, confirming that thiophene interacts with the Brönsted acid sites of HY, in agreement with that reported previously (Chica *et al.*, 2005, Garcia & Lercher, 1992, Geobaldo *et al.*, 1999, Shan *et al.*, 2002).

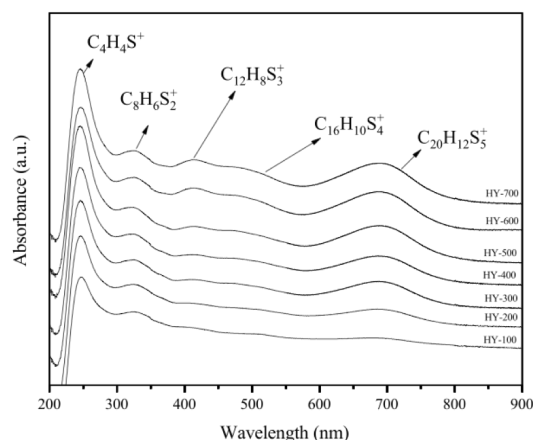


Fig. 3. UV-Vis spectra: Protonic Zeolite-Y (HY) after the adsorption of thiophene (HY-100-700). The spectrum of HY was subtracted from these spectra.

3.2 Formation of oligomeric species (UV-Vis)

After the adsorption process, the materials were characterized by UV-Vis spectroscopy to obtain indirect information about the structures of species adsorbed in zeolites HY and NaY. Figures 3 and 4 show the UV-Vis spectra corresponding to HY and NaY, respectively.

The UV-VIS spectrum of HY zeolite in contact with thiophene showed five absorption bands (~ 250 , ~ 340 , ~ 410 , ~ 500 y ~ 680 nm), which intensify as the initial concentration of thiophene increases in solution and is related with an increase of red tonality in the material. These bands agree with those previously reported (Geobaldo *et al.*, 1999; Caspar *et al.*, 1991; Valencia *et al.*, 2016) where the authors suggest that ~ 250 nm band corresponds to protonated thiophene monomer; ~ 340 nm band to protonated dithiophene; the optical transition of ~ 410 nm is assigned to protonated trithiophene formed by the interaction of three thiophene molecules (Caspar *et al.*, 1991; Geobaldo *et al.*, 1999); ~ 500 nm band to protonated tetrathiophene; while, the last band (~ 680 nm) is assigned to protonated pentathiophene. It should be noted that these last signals were assigned according to recent reports done by Valencia *et al.* (2016). In Fig. 7, the proposals of the mechanistically correct structures of oligomeric cations just mentioned are shown, which differ from those reported in the literature (Geobaldo *et al.*, 1999), discussed below.

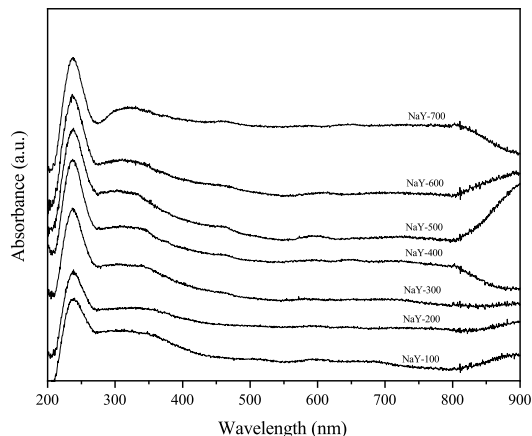


Fig. 4. UV-Vis spectrum: Sodic Zeolite-Y (NaY) after the adsorption of thiophene (NaY-100-700). The spectrum of NaY was subtracted from these spectra.

In the case of NaY, the UV-Vis spectrum has a broad band at ~ 240 nm with a slight displacement of 10 nm in relation to the HY band (~ 250 nm; Fig. 4), attributable to the possible overlap of bands from physisorbed thiophene in the Lewis acid sites, and to the protonated thiophene by the Brönsted acid site. The latter has been deduced from the assignments UV-Vis proposed by Geobaldo *et al.* (1999) and Caspar *et al.* (1991); and from a study made by Pang *et al.* (2007), on the interactions of thiophene with both, Lewis and Brönsted acid sites, who argue that the Brönsted acidity benefits the cracking activity and the Lewis acidity could facilitate the physisorption of thiophene molecules. The spectrum also showed a small band in ~ 340 nm zone, which is attributed to protonated dithiophene. As mentioned above, NaY maintains a fraction of Brönsted acid sites, causing the protonation of thiophene within NaY. This is agree with the change of color in the sample, which only reaches a straw yellow, without getting the typical intense red of colorful species, found in cationic thiophene oligomers. This confirms that in absence of Brönsted acid sites, the cationic oligomer is not formed (Fig. 7), and therefore, oligomerization is inhibited.

3.3 Oligomerization mechanism

It is known that acid zeolites can protonate unstable species (Bordiga *et al.*, 1993; Geobaldo *et al.*, 1999) by electrophilic attack of the Brönsted acid sites to molecules with π -bonds; forming cationic monomers, as is the case of protonated thiophene species ($T^- \cdots HY^+$) mentioned above.

These protonated species can continue to react with the same monomer to produce a sequential oligomerization, following the scheme for olefinic and acetylenic hydrocarbons described by Geobaldo *et al.* (1999) and Bordiga *et al.* (1993) (Fig. 5).

It is proposed that protonation occurs by attack to the electron pair of sulfur in the thiophenic ring (Fig. 6). The hydrogen bond in the $T \cdots HY$ specie is the precursor of protonated species ($T^+ \cdots HY^-$), whose structure is shown in the reaction route proposed in Fig. 6.

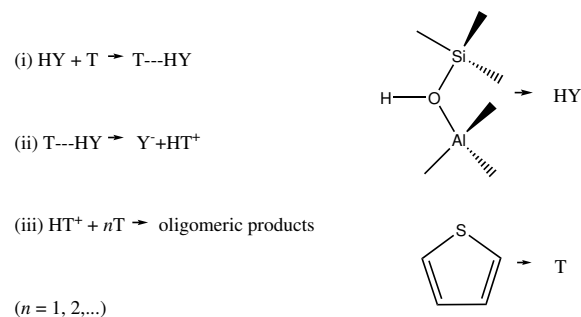


Fig. 5. Oligomerization reaction scheme (Geobaldo *et al.*, 1999).

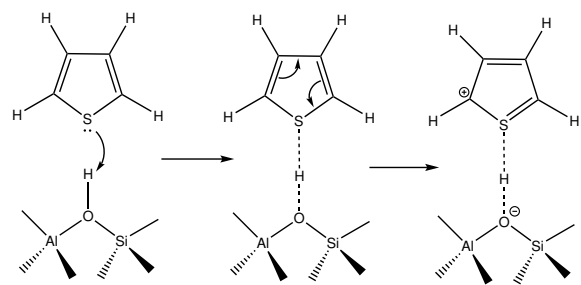


Fig. 6. Protonation of thiophene by HY.

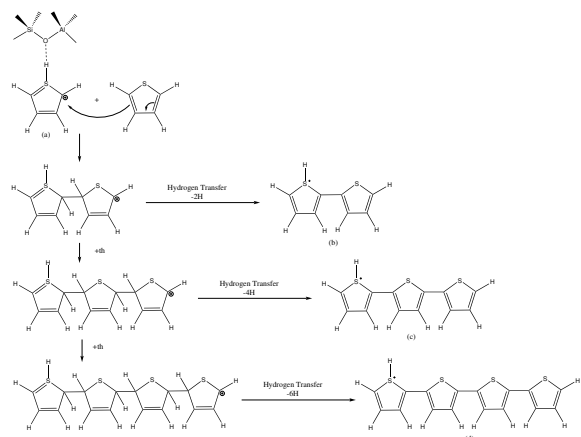


Fig. 7. Cation oligomer formation reaction route, (a) $C_4H_4S^+$, (b) $C_8H_6S_2^+$, (c) $C_{12}H_8S_3^+$ and (d) $C_{16}H_{10}S_4^+$. (Th \rightarrow Thiophene)

An excess of thiophene, can increase the protonated thiophene species chain length forming positively charged thiophene oligomers (Fig. 5 (iii)). The structure of protonated oligomeric species presented in Fig. 7 differs from those proposed by Geobaldo *et al.* (1999). It is suggested that the route proposed here correctly represents the chemistry involved.

The formation of cationic dithiophene, trithiophene, tetrathiophene and pentathiophene is demonstrated by the increase in band intensity at ~ 340 nm, ~ 410 nm, ~ 500 nm and ~ 680 nm, respectively, that increase with the initial concentration of thiophene added (Figure 3). The variation of spectra is directly related to the color of samples, which changes from yellow straw to a deep red after two hours.

These results agree with the reported by Yang *et al.* (2001) and Geobaldo *et al.* (1999) and is due to thiophene oligomeric species formed during the interaction of HY zeolite with the problem solution. It should be noted that the final specie formed, which remain stable within the zeolitic cavity, is protonated in sulfur and not in carbon, as previously reported by other authors (Valencia *et al.*, 2016) (Fig. 7), and was corroborated by ^{13}C Nuclear Magnetic Resonance spectroscopy presented below.

3.4 Nuclear Magnetic Resonance

The structure of the thiophene oligomers within the cavities of HY was analyzed by solid-state ^{13}C Nuclear Magnetic Resonance spectroscopy (^{13}C -NMR). The spectrum obtained after the adsorption process is shown in Fig. 8. Simulations were performed in the ACD Lab 3.5 program for ^{13}C -NMR to compare them with the obtained for HY. Based on this, it can be seen that the signal at ~ 125 ppm corresponds to aromatic CH of thiophene and thiophene oligomers, while the ~ 144 ppm signal corresponds to the ipso-quaternary carbons of thiophene oligomers. It is important to emphasize that there is no signal in lower fields at ~ 144 ppm, corresponding to carbocation ion proposed in the literature, which allow us to attribute the positive charge of molecules trapped within the cavity of HY zeolite, to sulfur of thiophene oligomeric chain that interacts with the Brönsted acid site, as can be seen in Fig. 7. Moreover, this configuration maintains the characteristic of electron delocalization throughout the structure of oligomeric species, favoring their semiconductor character.

On the other hand, in addition to the signals corresponding to thiophene and its oligomeric derivatives, a broad signal was observed in the range of ~25 to ~50 ppm, which corresponds to carbons with sp^3 hybridization. Due to the wide range of the signal, it is complicated to assign it to specific hydrocarbon molecules. However, the reaction route proposed by Shan *et al.* (2002) and Chica *et al.* (2005) (Fig. 9), shows the formation of thiols with double bonds, by rupture of the thiophenic ring, which react with each other forming more complex hydrocarbon molecules. However, the ^{13}C -NMR spectrum has no assignable signals to carbons with double bonds (Fig. 8). So, it is possible that these chains are saturated with hydrogen, forming thiols with saturated carbons, species that are detected in the ^{13}C -NMR spectrum shown in Fig. 8. The hydrogen necessary to saturate the double bonds comes from the released when the thiophene oligomers are formed (Fig. 7).

It is also of interest to point out that when the HY samples were contacted with thiophene, the characteristic smell of H_2S was detected. A qualitative test was carried out with a paper impregnated with silver nitrate, which upon contact with the vapors evolved from the adsorption of thiophene in the zeolite-Y, the characteristic black precipitate of Ag_2S was observed, which indicates the presence of H_2S .

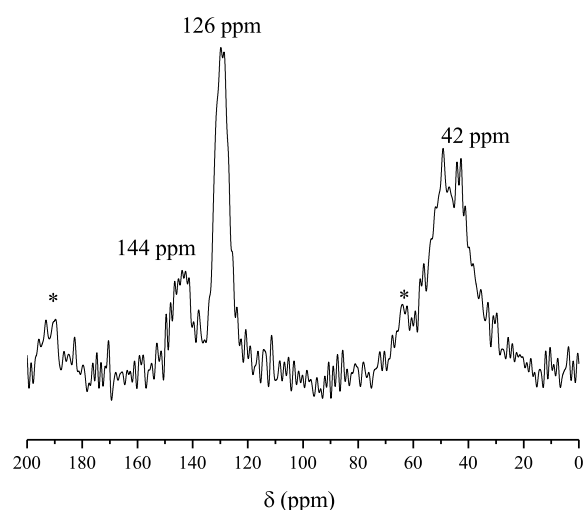


Fig. 8. ^{13}C -NMR spectrum: Protonic Zeolite Y (HY) after adsorbing thiophene in the vapor phase. The asterisk represents the rotation bands (SSB, Spinning SideBand).

The HY sample obtained after the thiophene adsorption process was washed with deuterated chloroform. From this solution, the Proton Nuclear Magnetic Resonance spectrum (^1H -NMR) in liquid phase was determined. The main compound obtained from the extraction corresponds to the molecule shown in Fig. 10, which was deduced from the ^1H -NMR spectrum, as well as from the correlations of the experiments COSY, HSQC and HMBC Gradients. Apparently, this type of species are formed outside the cavities of zeolite, since the structure prevents its formation inside that, therefore, it can be extracted by washing with chloroform. In addition, because the external surface is small, its abundance is much lower than the oligomers and hydrocarbons with sp^3 carbons. Additionally, the solid, previously washed with deuterated chloroform was again analyzed by ^{13}C -NMR, showing that the spectrum is very similar to that obtained in Figure 8, so, chloroform does not extract or modify the molecules formed within the cavities of the HY.

A series of additional NMR tests were also performed with NaY and H-ZSM5 after adsorption of thiophene in the gas phase (support material). The ^{13}C -NMR spectrum for NaY only showed the signal assigned to thiophene (~125 ppm), that is expected since NaY has few Brönsted acid sites.

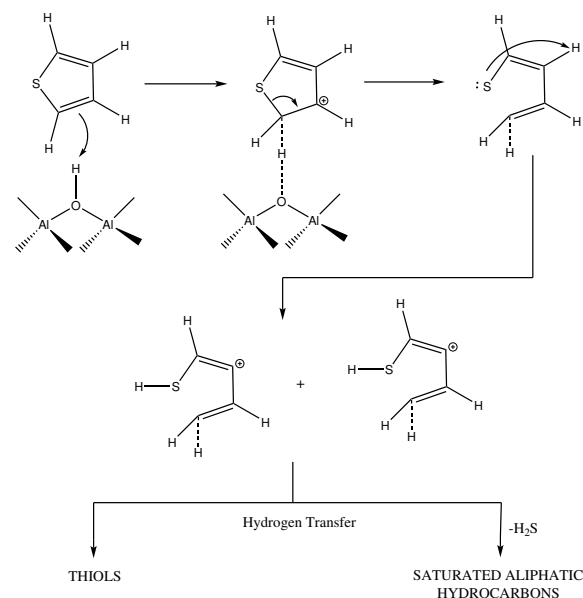


Fig. 9. Reaction route that shows the formation of thiols and saturated aliphatic hydrocarbons by the opening of thiophenic ring (Chica *et al.*, 2005; Shan *et al.*, 2002).

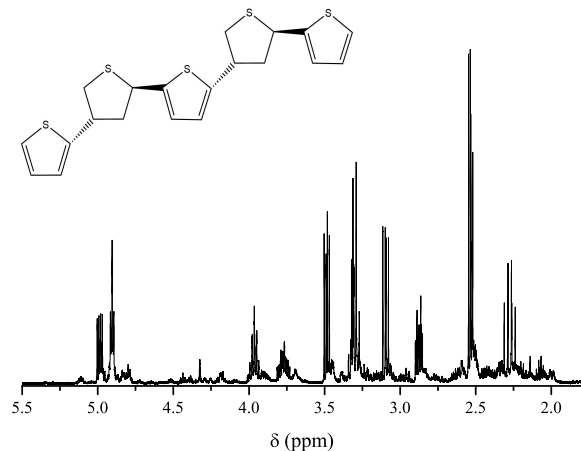


Fig. 10. ^1H -NMR spectrum in liquid state: Extraction with deuterated chloroform of Protonic Zeolite-Y (HY) after the process of thiophene adsorption in the gas phase. Expansion of the original spectrum of the region from 2 to 5.5 ppm. And the molecule to which the corresponding signals of this spectrum are assigned.

In the case of H-ZSM5, the color change was similar to NaY, and the ^{13}C -NMR spectrum presented a signal corresponding to thiophene (~ 125 ppm) and a small signal representative of carbons with sp^3 hybridization of the aliphatic hydrocarbons (~ 42 ppm). This latter can be explained if we consider that H-ZSM5 has lowest Brönsted acidity (Si/Al=35) than HY (Si/Al=1.6); indicating that protonic zeolite with high Si/Al ratio is not suitable for the thiophene oligomerization since it enhances the Lewis acidity (Colín-Luna *et al.*, 2013), and consequently, the physisorption of monomer.

Conclusions

The IR spectra of the materials analyzed indicates that the interaction with thiophene occurs through the Brönsted acid sites, which justifies the physical interaction of thiophene with NaY. The UV-Vis analysis of the HY shows signals assignable to oligomeric species of the type dithiophene, trithiophene, tetrathiophene and pentathiophene, whose intensity increases with the initial concentration of thiophene. In the case of NaY, the UV-Vis spectrum indicates that only protonated thiophene is formed,

in addition to the unprotonated thiophene adsorbed. The ^{13}C -NMR spectrum of HY not only corroborates the presence of oligomeric species of thiophene, but also presents an assignable signal to carbons with sp^3 hybridization in saturated hydrocarbons. Due to the wide of signal it is not possible to assign it to specific structures.

The reactions between the Brönsted acid sites of HY and thiophene at room temperature can occur in two ways, originating two groups of molecules:

(a) The interaction of free electron pair of sulfur in thiophene with the Brönsted acid site ($\eta^1\text{S}$ interaction) (Ma *et al.*, 2002; Song and Ma, 2003) induces the formation of thiophene oligomeric species, stopping the process of sequential oligomerization in the pentathiophene (Fig. 11).

(b) The interaction of α -carbon of the thiophene molecule with the Brönsted acid site (interaction $\eta^1\text{C}$) (Ma *et al.*, 2002; Song & Ma, 2003) causes the thiophenic ring to be opened by breaking the $\text{C}_\alpha\text{-S}$ bond (Fig. 11). The resulting specie reacts with another molecule of the same type leading to the formation of H_2S , thiols and hydrocarbons with sp^3 carbons; the latter is produced by breaking the C-S bond of thiols.

The ^1H -NMR spectrum of deuterated chloroform used to extract hydrocarbons from the HY zeolite containing thiophene oligomeric species shows that only a very small fraction is extractable. Consequently, most oligomers are formed within the pores of zeolite, and are trapped due to steric constraints.

The results presented here shows that interaction between the protonic zeolite and thiophene is chemical and not only physical as proposed by several authors (Yang *et al.*, 2001). The species that are formed have a complex structure (oligomers) and are trapped inside the cavities of zeolite, these species become charged in the sulfur that interacts with the Brönsted acid site. However, there is a drawback, oligothiophenes are trapped within the zeolitic structure and their extraction requires complicated methods like treatments at high temperatures, until now, still under study. Possible applications of the materials are also in analysis without the need to extract the oligomers from the zeolitic cavities; we work on a hybrid material with TiO_2 , since the presence of sulfates on this materials provide catalytic stability and has a remarkable influence in the selectivity and performance of the reaction (Cruz-Ortiz *et al.*, 2017).

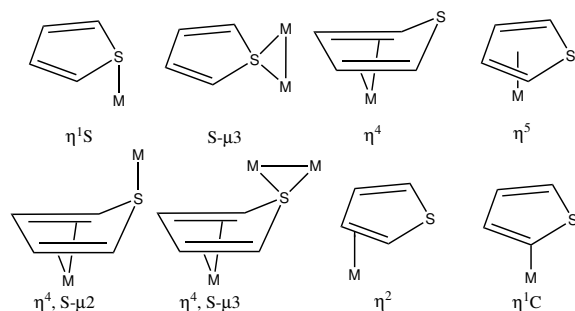


Fig. 11. Known geometric coordinates of thiophene with metal species in organometallic complexes, indicating the possible configurations of thiophene adsorption on the surface of adsorbents. Taken from the work of Song and Ma (2003).

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References

Bäuerle, P. (2008). The Synthesis of Oligothiophenes. In Fichou, D. (Ed.) *Handbook of Oligo- and Polythiophenes*. John Wiley & Sons.

Becker, R. S., Seixas de Melo, J., Macanita, A. L., & Elisei, F. (1996). Comprehensive evaluation of the absorption, photophysical, energy transfer, structural, and theoretical properties of α -oligothiophenes with one to seven rings. *The Journal of Physical Chemistry* 100, 18683-18695.

Bordiga, S., Ricchiardi, G., Spoto, G., Scarano, D., Carnelli, L., Zecchina, A., & Areán, C. O. (1993). Acetylene, methylacetylene and ethylacetylene polymerization on H-ZSM5: A spectroscopic study. *Journal of the Chemical Society, Faraday Transactions* 89, 1843-1855.

Breck, D. W. (1974). *Zeolite Molecular Sieves: Structure, Chemistry and Use*, John Wiley and Sons, Inc., New York, Malabar, Florida.

Brütting, W. (Ed.). (2006). *Physics of Organic Semiconductors*. John Wiley & Sons.

Caspar, J. V., Ramamurthy, V., & Corbin, D. R. (1991). Preparation and spectroscopic characterization of polarons and bipolarons of thiophene oligomers within the channels of pentasil zeolites: the evolution of organic radical ions into conducting polymers. *Journal of the American Chemical Society* 113, 600-610.

Cerqueira, H. S., Caeiro, G., Costa, L., & Ribeiro, F. R. (2008). Deactivation of FCC catalysts. *Journal of Molecular Catalysis A: Chemical* 292, 1-13.

Chica, A., Strohmaier, K. G., & Iglesia, E. (2005). Effects of zeolite structure and aluminum content on thiophene adsorption, desorption, and surface reactions. *Applied Catalysis B: Environmental* 60, 223-232.

Colín-Luna, J. A., Medina-Mendoza, A. K., De los Reyes, J. A., Escobar, J., Montoya de la Fuente, J. A. & Suarez P., R. (2013). Effect of Si/Al ratio in deep hydrodesulfurization of Pt/Al-MCM41 catalysts. *Revista Mexicana de Ingeniería Química* 12, 271-282.

Coropceanu, V., Cornil, J., da Silva Filho, D. A., Olivier, Y., Silbey, R., & Brédas, J. L. (2007). Charge transport in organic semiconductors. *Chemical Reviews* 107, 926-952.

Cruz-Ortiz, B. R., Díaz-Jiménez, L., Cortés-Hernández, D. A. & Múzquiz-Ramos, E. M. (2017). TiO₂ catalysts used in claus processes: deactivation causes and catalytic activity. *Revista Mexicana de Ingeniería Química* 16, 229-236.

García, C. L., & Lercher, J. A. (1992). Adsorption and surface reactions of thiophene on ZSM 5 zeolites. *The Journal of Physical Chemistry* 96, 2669-2675.

Geobaldo, F., Palomino, G. T., Bordiga, S., Zecchina, A., & Areán, C. O. (1999). Spectroscopic study in the UV-Vis, near and mid IR of cationic species formed by interaction of thiophene, dithiophene and terthiophene with the zeolite HY. *Physical Chemistry Chemical Physics* 1, 561-569.

Hernández-Maldonado, A. J., & Yang, R. T. (2004). Desulfurization of diesel fuels by adsorption via π -complexation with vapor-phase exchanged Cu(I)- Y zeolites. *Journal of the American Chemical Society* 126, 992-993.

- Hernández-Maldonado, A. J., Stamatis, S. D., Yang, R. T., He, A. Z., & Cannella, W. (2004). New sorbents for desulfurization of diesel fuels via π complexation: layered beds and regeneration. *Industrial & Engineering Chemistry Research* 43, 769-776.
- Ma, X., Sun, L., & Song, C. (2002). A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. *Catalysis Today* 77, 107-116.
- Mishra, A., Ma, C. Q., Segura, J. L., & Bäuerle, P. (2009). Functional oligothiophene-based materials: nanoarchitectures and applications. In Perepichka, I. F., & Perepichka, D. F. (Eds.). (2009). *Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics*, 2 Volume Set. John Wiley & Sons. Pp 1-155.
- Pang, X., Zhang, Li., Sun, S., Liu, T. & Gao, X., (2007). Effects of metal modifications of Y zeolites on sulfur reduction performance in fluid catalytic cracking process. *Catalysis Today*, 125, 173-177.
- Schulz, H., Böhringer, W., Ousmanov, F., & Waller, P. (1999a). Refractory sulfur compounds in gas oils. *Fuel Processing Technology* 61, 5-41.
- Schulz, H., Böhringer, W., Waller, P., & Ousmanov, F. (1999b). Gas oil deep hydrodesulfurization: refractory compounds and retarded kinetics. *Catalysis Today* 49, 87-97.
- Shan, H. H., Li, C. Y., Yang, C. H., Zhao, H., Zhao, B. Y., & Zhang, J. F. (2002). Mechanistic studies on thiophene species cracking over USY zeolite. *Catalysis Today* 77, 117-126.
- Shirakawa, H., Louis, E. J., MacDiarmid, A. G., Chiang, C. K., & Heeger, A. J. (1977). Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH) x. *Journal of the Chemical Society, Chemical Communications* 16, 578-580.
- Song, C., & Ma, X. (2003). New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Applied Catalysis B: Environmental* 41, 207-238.
- Takahashi, A., Yang, F. H., & Yang, R. T. (2002). New sorbents for desulfurization by π -complexation: thiophene/benzene adsorption. *Industrial & Engineering Chemistry Research* 41, 2487-2496.
- Uytterhoeven, J. B., Christner, L. G., & Hall, W. K. (1965). Studies of the hydrogen held by solids. VIII. The decationated zeolites. *The Journal of Physical Chemistry* 69, 2117-2126.
- Uytterhoeven, J. B., Jacobs, P., Makay, K., & Schoonheydt, R. (1968). The thermal stability of hydroxyl groups in decationated zeolites X and Y. *The Journal of Physical Chemistry* 72, 1768-1775.
- Valencia, D., Whiting, G. T., Bulo, R. E., & Weckhuysen, B. M. (2016). Protonated thiophene-based oligomers as formed within zeolites: understanding their electron delocalization and aromaticity. *Physical Chemistry Chemical Physics* 18, 2080-2086.
- Whiting, G. T., Meirer, F., Valencia, D., Mertens, M. M., Bons, A. J., Weiss, B. M., Stevens, P. A., Smit, E., & Weckhuysen, B. M. (2014). Selective staining of Brønsted acidity in zeolite ZSM-5-based catalyst extrudates using thiophene as a probe. *Physical Chemistry Chemical Physics* 16, 21531-21542.
- Yang, R. T., Takahashi, A., & Yang, F. H. (2001). New sorbents for desulfurization of liquid fuels by π -complexation. *Industrial & Engineering Chemistry Research* 40, 6236-6239.