Ab Initio Screening of Zeolite Y Formulations for Efficient Adsorption of Thiophene in Presence of Benzene

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ABSTRACT

In the context of deep desulfurization of transport fuels, the present work aimed at identifying a suitable material for the selective removal of thiophene from fuels. Dispersion corrected density functional theory (DFT) calculations have been carried out in order to investigate the adsorption of benzene and thiophene in various faujasite zeolite formulations including DAY, HY, LiY, NaY, KY, CsY, Cu(I)Y, Cu(II)Y, Ag(I)Y, Zn(II)Y, and FAU containing Lewis acid sites (LAS) (defect or extra-framework). Bearing-LAS FAU, Cu(I)Y, Cu(II)Y, Zn(II)Y, CsY, and HY showed a higher affinity towards thiophene adsorption. In particular, thiophene is more adsorbed on defect LAS than benzene by 17.7 kJ/mol, suggesting that this zeolite could be chosen as a suitable candidate for the optimal selective adsorption of thiophene in the presence of benzene. In terms of regenerability, all formulations can be safely used (except the one containing extra-framework Lewis acid sites) as they can limit the activation of the C-S bond of thiophene. Considering both adsorption selectivity and sorbent regenerability criteria, faujasites containing defect Lewis acid sites could be chosen as a good compromise to perform a selective adsorption of thiophene in presence of benzene.

Keywords: Desulfurization, porous, cation, faujasite, DFT, sulfur

1. Introduction

The environmental legislation of many countries requires a reduction of the sulfur contents of gasoline and diesel fuels from 400-500 to 0.1-0.2 ppm [1–3], since sulfur-bearing compounds present in commercial fuels contribute to catalyst poisoning during petroleum refining, and to toxic SO_x emissions during fuel combustion in vehicles [4,5]. Thus, deep desulfurization of transport fuels is currently a major world research topic [6–9]. Several efficient technologies already exist such as hydrodesulfurization (HDS) [10,11], extractive desulfurization (EDS) [12], reactive adsorption desulfurization (RADS) [13], oxidative desulfurization (ODS) [14], and adsorptive desulfurization (ADS) [15]. Sulfur compounds are present in fuels as thiols, thioethers and thiophenic species. HDS appears as an efficient technology for thiol and thioether removal, but the process is inefficient for the elimination of thiophenic compounds such as 4,6-dimethyldibenzothiophene which is the most refractory compound to HDS [16]. Moreover, HDS can generate H_2S, which is inhibitory for the deep hydrodesulfurization of the most refractory compounds [17]. Adsorption desulfurization (ADS) can be considered as one of the most promising processes to ultra-clean diesel and gasoline under moderate conditions (ambient temperature and atmospheric pressure) [4,8,15,16,18–21]. Its success is due to the development of highly selective sorbents showing a higher affinity for sulfur compounds than for other major fuel components, and to other criteria such as an excellent adsorption capacity and good sorbent reusability [20–25]. However, the adsorption of sulfur species on sorbents undergoes a strong competition on the adsorption sites with desired aromatics, such as benzene. Commercially available sorbents tested are zeolites, activated charcoal, and activated alumina [26–31]. The zeolite ZSM-5 was shown to be more selective for thiophene than for benzene, toluene, and p-xylene [32]. However, its limited pore size (5.2 to 5.6 Å [33]) sterically hinders or excludes the adsorption of bulky sulfur compounds presenting more than one aromatic ring. Faujasite type zeolites (FAU) which have larger pore sizes and

volumes should be more suitable than ZSM-5 for the adsorption of aromatic sulfur compounds. They present a large supercage of 11.0 x 13.0 Å with a large pore opening of 7.4 x 7.4 Å, numerous adsorption sites in the supercages, and excellent thermal stability [6,8,34–37].

To be selected for ADS technology, sorbents need to combine both high selectivity and good regeneration ability. These two criteria can be estimated by determining the sorbent affinity for various desirable and undesirable molecules present in fuels. Using molecular orbital (MO), Yang et al. [38] investigated π-complexation between thiophene/benzene and transition metals. They also explored the selectivity and reversibility of π-complexation. However, the interactions between thiophene and transition metals are governed by π-complexation, which makes its separation from aromatic hydrocarbons too difficult. Moreover, numerous studies have shown a strong competition between aromatic and thiophenic compounds [17,19,28] for adsorption on various sorbents such as H-ZSM5, H-Beta, HY, AgY, CuY, NaY, H-USY, Na-ZSM-5, activated carbon, and modified activated alumina. Experimental studies have demonstrated that benzene [8] and toluene [39,40] inhibit the adsorption of thiophene in HY zeolites. Using nine types of zeolites, including FAU, FER, and MFI, Zeng et al. [17] investigated the selective adsorption of thiophene in the presence of benzene as a model for aromatic molecules, and showed a strong competition between benzene and thiophene. In fact, in binary mixtures, the sorbent selectivity for thiophene highly depends on pore size, with the optimum pore diameter being between 4.6 and 5.0 Å. In the same context, Duan et al. [18] showed that the efficiency of sulfur compounds removal decreased in the presence of benzene and o-xylene. Using several sorbents including Ag-Y, Cu-Y, Na-Y, H-USY, Na-ZSM-5, activated carbon, and modified activated carbon, Takahashi et al. [28] experimentally investigated benzene/thiophene adsorption. They reported excellent adsorption performances

in terms of adsorption and separation capacity for Cu-Y and Ag-Y. However, these results were given without molecular explanations.

Density Functional Theory (DFT) calculations have been widely used for identifying suitable zeolite formulations for selective trapping applications such as phenol separation from toluene for the purification of biofuels [34,41–44], trapping of iodine species released during nuclear incidents [45–47], and the separation of NO_x and CO from H_2O and CO_2 for the prevention of harmful emissions from diesel engines in confined spaces [48].

The present work aims at providing new insights into the capture of thiophene by FAU type zeolites in the presence of benzene, using dispersion corrected periodic DFT calculations, with taking in account van der Waals (vdW) interactions. More precisely, our objectives are to highlight the influence of the compensating charge cation of the zeolite for thiophene adsorption, and to identify the most efficient FAU formulation, in terms of selectivity and regenerability, for thiophene adsorption in the presence of benzene. Selected formulations are as follows: DAY (Si/Al=∞), D-LAS (Defect Lewis acid site of a Faujasite) [41], EX LAS (Extra-framework Lewis acid site) [41], and the cationic forms HY, LiY, NaY, KY, CsY, Cu(I)Y, Ag(I)Y, Zn(II)Y, Cu(II)Y (Si/Al ratio of 2.43). To our knowledge, there is no DFT investigation dedicated to this issue.

The present paper is organized as follows: the first part describes in details our computational procedure; the second part presents and discusses the obtained results, with focusing on the potential inhibitory effect of benzene on thiophene adsorption; finally, the third and last part outlines the main conclusions of the present work.

2. Computational details

2.1 Methods

Thiophene and benzene adsorption onto FAU zeolites were investigated using the Vienna Ab-initio Simulation Package (VASP) [49]. For these tasks, our DFT calculations employed the PBE functional and projector augmented plane wave (PAW) method [50,51] with a chosen plane wave cutoff energy of 450 eV. Kohn-Sham equations were solved iteratively until the energy difference between cycles became lower than 10^{-6} eV, while the Gaussian smearing was fixed to 0.1 eV. Sampling of the Brillouin zone was limited to the Γ-point. FAU structures were entirely optimized until all the forces fall below 0.01 eV/Å per atom. In order to account for the vdW interactions, the PBE+TS/HI level of theory [52,53] was used. This method has been proven to describe accurately ionic systems such as cationic zeolites [41,48,54]. Adsorption phenomena were evaluated with determining the interaction energy ΔE_{int} between a molecule and a FAU formulation, as indicated in our previous works [54–59].

2.2 Structural model

The FAU structure is made up of cuboctahedron sodalite units connected to each other by hexagonal prisms (D6R), leading to the formation of large empty cavities well known as supercages. Interconnections between supercages and their hexagonal windows (6MR) form the porosity of the FAU structures. The pure siliceous structure (DAY) is crystallized within the Fd3m symmetry space group [60] and its supercell structure has the lattice parameters of a=b=c =25.028 Å (576 atoms, $Si_{192}O_{384}$) and $\alpha = \beta = \gamma = 90°$ [61]. By means of the DFT approach, it is difficult in terms of current computational efforts to study the FAU supercell. Therefore, primitive rhombohedral FAU have been used, containing only 144 atoms and represented by two supercages and eight hexagonal windows connecting sodalite cages with supercages, in line with previous studies [62–64]. Twelve FAU structures have been investigated, namely DAY, cation exchange faujasites MY (Si/Al=2.43), where M= H, Li, Na, K, Cs, Cu (I), Ag (I), Zn (II), Cu (II), D-LAS and EX-LAS. DAY is a pure siliceous

structure with a Si/Al ratio of ∞ exhibiting a high hydrophobicity [65]. D-LAS is modeled by an excess of negative charge around the placement of the atoms of AlO_4 in FAU (Si/Al = 47; resulting from a simple substitution of Si^{4+} by Al^{3+}) [41,66], while EX-LAS is represented by the substitution of the three Si^{4+} by three Al^{3+} in a 6MR window, and the addition of an extra framework Al^{3+} cation in order to achieve total neutrality in FAU [41].

3. Results and discussion

3.1. Adsorption of benzene and thiophene in FAU zeolites

The present part provides a systematic DFT investigation of thiophene and benzene adsorption on the following FAU formulations: DAY, D-LAS and EX-LAS Lewis acid site models, and MY (where M= H, Li, Na, K, Cs, Cu (I), Ag (I), Zn (II), Cu (II)). Calculations were performed using the TS/HI level of theory (PBE+TS/HI). Adsorption configurations are reported in Table S1 (supporting information) and Fig. 1, while total interaction energies are shown in Table 1 and Fig. 2.

3.1.1. Adsorption of thiophene

In DAY, both the sulfur atom and the aromatic ring contribute together to the adsorption of thiophene with ΔE_{int} of 41.5 kJ/mol. This adsorption is controlled by the interactions of the center of a 6MR window of DAY with carbon atoms in thiophene at distances of 3.70-3.94 Å, and with the sulfur atom at a distance of 4.21 Å. For any other FAU formulation, ΔE_{int} thiophene is between 2 and 4 times higher than for DAY.

In HY, ΔE_{int} of thiophene is of 90.9 kJ/mol. This adsorption is governed by the interactions of the protonated sites in HY, with the sulfur atom at a distance of 3.29 Å, and with carbons at distances of 2.13 to 3.81 Å (Table S1).

For LiY, NaY, KY, and CsY, ΔE_{int} of thiophene are of 64.6 kJ/mol, 76.2 kJ/mol, 81.6 kJ/mol, and 99.2 kJ/mol, respectively. These results indicate a particular behavior where the total

interaction energy of thiophene with alkali-FAU increases with the size of the alkali cation. Moreover, our results are in agreement with Takahashi *et al.* [28] who indicated adsorption enthalpies of thiophene in H-USY (high Si/Al) and NaY at room temperature of 46 and 82 kJ/mol, respectively. Adsorption configurations show that Li^+, Na^+, K^+ and Cs^+ interact with thiophene via the sulfur atom at distances of 3.38 Å, 3.15 Å, 3.42 Å and 3.79 Å respectively, and via its carbons at distances of 2.50-3.20 Å, 2.80-3.00 Å, 3.17-3.45 Å, 3.58-3.79 Å, respectively (Table S1). The exchange of alkali cations with transition metal cations (Cu(I), Cu(II), Ag(I), or Zn(II)) results in a significant increase in the affinity of thiophene for FAU zeolites as shown by ΔE_{int} which are of 138.8 kJ/mol for Cu(I), 79.3 kJ/mol for Cu(II)Y, 107.3 for Ag(I)Y, and 123.5 kJ/mol for Zn(II)Y. Our results are in agreement with those obtained by Oliveira et al. [67] which indicated a strong adsorption of thiophene on transition metals by comparison with the Na^+ cation. In these sorbents, cationic transition metals Cu(I), Cu(II), Zn(II), and Ag(I) interact with the sulfur atom of thiophene at distances of 3.12 Å, 3.71 Å, 3.29 Å, and 3.33 Å respectively, and with its carbons at distances of 2.01-3.40 Å, 3.02-3.68 Å, 2.27-3.71 Å, and 2.37-3.58 Å, respectively (Table S1).

For D-LAS and EX-LAS formulations, ΔE_{int} of thiophene are of 112.1 kJ/mol and 172.9 kJ/mol, respectively. The highest adsorption energy of thiophene is observed with EX-LAS. Considering D-LAS, its 6MR structure interacts with thiophene via the sulfur atom at a distance of 3.76 Å, and also via carbons at distances of 2.86-3.85Å. EX-LAS interacts with the sulfur atom of thiophene at a distance 3.14 Å and also with its carbons at distances of 2.13-3.87Å. Moreover, interactions between EX-LAS and thiophene are closer than those observed between D-LAS and thiophene, showing that thiophene interacts more closely with EX-LAS than with D-LAS.

These results show a strong affinity of thiophene for EX-LAS and Cu(I)Y. Interactions between thiophene and other zeolite formulations decrease in the following order: ZnY > D-

186 LAS ≈ Ag(I) > CsY ≈ HY. This trend is in good agreement with experimental data reported
187 by Takahashi et al. [28]. Moreover, other experimental data [67] have shown that thiophene is
188 more adsorbed on transition metals than on alkali metals.

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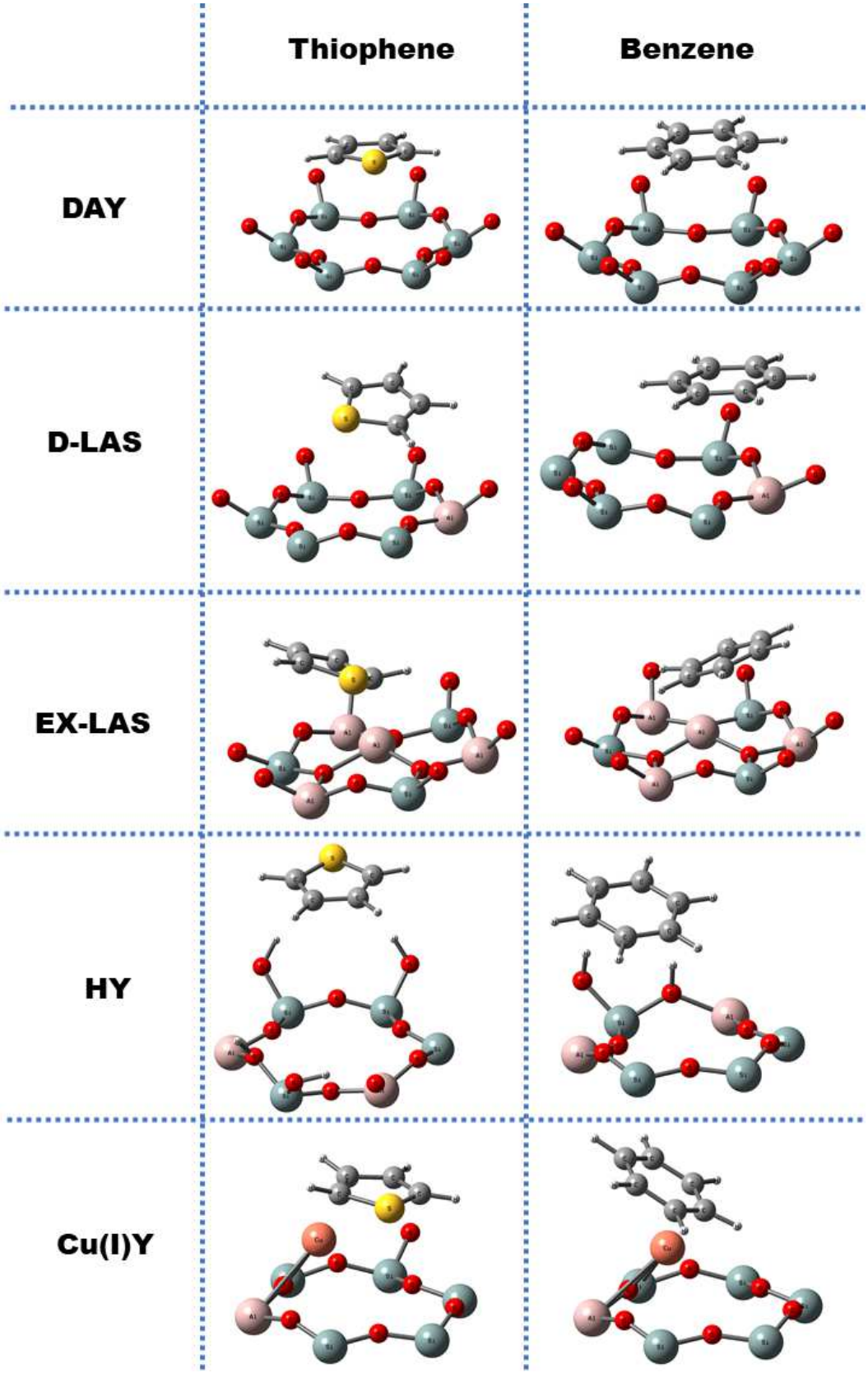

Fig. 1. Adsorption configurations of thiophene and benzene in DAY, HY, Cu(I)Y, D-LAS, and EX-LAS. For the sake of clarity, only the 6MR window surrounding the cation and the molecules is displayed. Blue, red, pink, white, gray and yellow balls represent silicon, oxygen, aluminum, hydrogen, carbon, and sulfur atoms, respectively.

Table 1. Computed total interaction energies. $|\Delta E_{int}$ (kJ/mol) $|$ of benzene and thiophene in DAY, MY (Si/Al=2.43) and FAU bearing either D-LAS (Si/Al=47) or EX-LAS (Si/Al=15).

	$\|\Delta E_{int}$(kJ/mol)$\|$	
	Thiophene	**Benzene**
DAY	41.5	48.5
D-LAS	112.1	94.4
EX-LAS	172.9	158.6
HY	90.9	85.7
LiY	64.6	73.5
NaY	76.2	89.2
KY	81.6	83.3
CsY	99.2	95.8
Cu(I)Y	138.8	131.4
Ag(I)Y	107.3	114.2
Zn(II)Y	123.5	116.8
Cu(II)Y	79.3	73.6

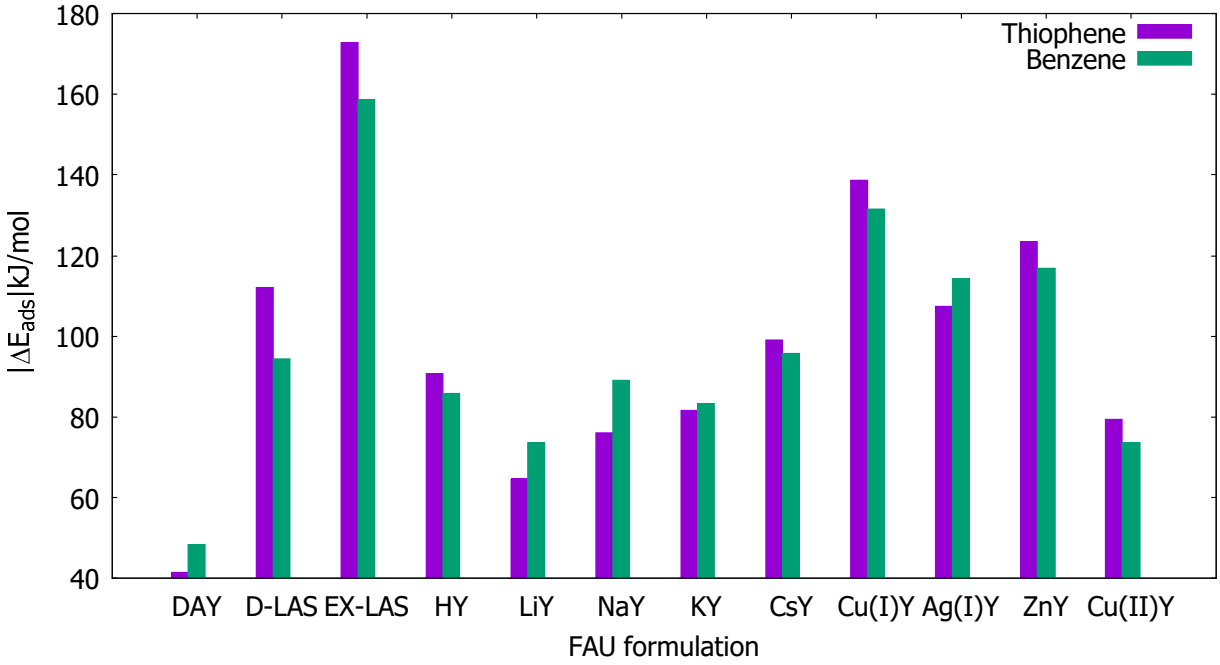

Fig. 2. Total interaction energies of thiophene and benzene molecules, in DAY, D-LAS-bearing FAU, EX-LAS-bearing FAU, HY, LiY, NaY, KY, CsY, Cu(I)Y, Ag(I)Y, Zn(II)Y, and Cu(II)Y.

3.1.2. Adsorption of benzene

In DAY, benzene interacts with the center of a 6MR window via its carbon atoms at distances of 3.58-3.93 Å. The total interaction energy calculated for benzene and DAY (48.5 kJ/mol) is

the lowest value observed. Indeed, FAU zeolites with any kind of charge compensating cation or Lewis acid site in their structure exhibit ΔE_{int} with benzene of about 2 to 3 times higher than for DAY. It is already known that the aromatic components can strongly interact over the zeolitic acid sites [68–72], as well as the adsorption strength of these molecules monotonically increases with the cation content [73,74].

For HY and NaY, the interaction energies with benzene are 85.7 kJ/mol and 89.2 kJ/mol, respectively. These values are respectively 37.2 and 40.7 kJ/mol higher than for DAY. For LiY, KY and CsY, ΔE_{int} with benzene are 73.5, 83.3, and 95.8 kJ/mol, respectively, which are respectively 25 to 47 kJ/mol higher than for DAY. This trend is consistent with an ONIOM (Own N-layered Integrated molecular Orbital and molecular Mechanics) study on the adsorption of benzene in alkali-exchanged FAU and ZSM-5 zeolites [75]. Moreover, experimental determinations of the adsorption enthalpy of benzene with NaY at room temperature estimated values of about 76 kJ/mol [76,77]. Since a correction of 10 kJ/mol is necessary for extrapolating the adsorption energy at 0 K to an adsorption enthalpy at 300 K [34], our calculations of the total interaction energy at 0K are in good agreement with experimental results. In HY, we found 2 protons interacting with carbons of the aromatic ring of benzene at distances of 2.15-3.50 Å (Table S1). However, Li^+, Na^+, K^+, and Cs^+ interact with carbons of the aromatic ring of benzene at distances of 2.60-2.93 Å, 2.85-2.88 Å, 2.98-3.39 Å, and 3.59-3.67 Å, respectively (Table S1).

For Cu(I)Y and Cu(II)Y, ΔE_{int} with benzene are 131.4 kJ/mol and 73.6 kJ/mol, respectively. These values are 82.9 kJ/mol and 25.1 kJ/mol higher than for DAY. In these cases, Cu(I) and Cu(II) cations interact with the carbon atoms of the aromatic ring of benzene respectively at distances of 2.04-3.23 Å, and 2.98-3.43 Å. Moreover, Cu (I) results in a higher total interaction energy than Cu (II), showing that the oxidation state of the copper cation has a clear effect on benzene adsorption in FAU. These results indicate that the interaction of

benzene with Cu(I) is more stable than with Cu(II). They are in accordance with Kung studies [78] which reported that at high oxidation states, metals act as weak Lewis acid sites, resulting in a weak interaction energy with adsorbed molecules. In addition, using FTIR spectra Archipov et al. [79] showed that copper undergoes a reduction from Cu(II) to Cu(I) during the adsorption of benzene.

For AgY and Zn(II)Y, ΔE_{int} with benzene are 114.2 kJ/mol and 116.8 kJ/mol, respectively. In these sorbents, Ag(I) and Zn(II) interact with carbons of the aromatic ring of benzene at distances of 2.38-3.59 Å and 2.39-3.61 Å, respectively (Table S1). Hence, transition metals Cu, Ag and Zn show a high total interaction energy with benzene, with Cu exhibiting the highest one. Again, our theoretical investigations are in agreement with previous experimental results indicating room temperature adsorption enthalpies of benzene with CuY and AgY of approximately 91.2 kJ/mol and 84.1 kJ/mol, respectively [28].

For D-LAS, the total interaction energy with benzene is 94.4 kJ/mol, which is 45.9 kJ/mol higher than for DAY. Finally, the highest ΔE_{int} of benzene is observed with EX-LAS (158.6 kJ/mol).

Therefore, benzene adsorption with FAU formulations decreased as follows: bearing-EX-LAS FAU > Cu(I)Y > Zn(II)Y ≈ Ag(I)Y > bearing-D-LAS FAU ≈ CsY > NaY > HY > KY > LiY ≈ Cu(II)Y > DAY. Benzene adsorption in different sorbents is performed through interactions between charge compensating cations or 6MR (in DAY) and the aromatic cycle of benzene (Table S1). Our present results are in line with some studies from the literature. Indeed, Takahashi et al. [28] combined experimental determinations and molecular orbital calculations for investigating the adsorption of benzene into several sorbents, including Ag-Y, Cu-Y, Na-Y, and H-USY. Their results showed that benzene highly adsorbs on Cu and Ag cations through π-complexation. Performing an experimental study, Archipov et al. [79]

suggested that benzene adsorption on transition metals is favored by Brønsted sites in Y zeolite.

3.2. Selectivity of thiophene adsorption on FAU zeolites in the presence of benzene

The previous results (parts 3.1.1. and 3.1.2.) provided individual details on the adsorption of thiophene and benzene in various zeolite formulations. Plotting the interaction energies of benzene and thiophene with the various sorbents (Fig. 2) allows a comparison of the sorbent affinities for these two molecules.

In HY, CsY, Cu(II)Y, Cu(I)Y, and Zn(II)Y, thiophene is slightly more adsorbed than benzene by 5.2 kJ/mol, 3.4 kJ/mol, 5.7 kJ/mol, 7.4 kJ/mol, 6.7 kJ/mol, respectively. However, in LiY, NaY, KY, and Ag(I)Y, benzene is slightly more adsorbed than thiophene by 8.9 kJ/mol, 13.0 kJ/mol, 1.7 kJ/mol, and 6.9 kJ/mol, respectively. Such energy differences are too low to conclude about the sorbent selectivity towards thiophene or benzene. On the other hand, thiophene is more adsorbed than benzene by 17.7 kJ/mol on D-LAS, suggesting an outstanding trapping performance for D-LAS towards thiophene. Similarly, EX-LAS could be a potential candidate for the selective adsorption of thiophene (energy difference of 14.3 kJ/mol). However, its interaction energy with thiophene (172.9 kJ/mol) might be too high to allow a straightforward regeneration of the sorbent.

In general, we can clearly suggest that the two zeolite formulations, D-LAS and EX-LAS, present a much higher affinity for thiophene than for benzene. They both display Lewis acid sites. Therefore, we suggest the use of zeolites with a large amount of Lewis acid sites for a selective trapping of thiophene in presence of benzene. Noteworthy, based on the results of our current paper, other theoretical approaches could be performed for a limited selection of formulations to study high coverage such as GCMC and MD simulations, and of course, dedicated experiments could also be performed.

3.3. Evaluation of the regenerability of zeolite formulations

In addition to the adsorption selectivity criterion, it is also necessary to consider the possibility of chemical reactions between adsorbed thiophene and the investigated formulations as well as the formation of by-products, which would reduce the trapping efficiency and then make the renegenability of the sorbent more difficult [80,81]. To check this point, we analyzed the length of the two S-C bonds ($S\text{-}C_1$ and $S\text{-}C_4$ as labeled in Fig. 3) in thiophene in its gaseous phase (before adsorption), and during adsorption over different formulations. Indeed, three possible situations can arise during adsorption: 1) the first S-C bond remains as in the gas phase (or decrease a little) and the second is lengthened, 2) both S-C bonds in thiophene are lengthened, 3) both S-C bonds keep the same distance during adsorption as in the gas phase. In the first two situations, the elongation of the S-C bond up to dissociation could result in the molecule destruction, and in completely modifying the degree of freedom of sulfur atoms. Ultimately, sulfur atoms of thiophene could be released and precipitate with chemical species present in the adsorption sites. On the other hand, in situation 1, breaking one S-C bond could allow the capture of the sulfur atom in the adsorption site, and facilitate breaking of the second S-C bond. In our investigations, analysis of the bond lengths before and after adsorption showed the following results:

- In EX-LAS, an elongation of the S-C bond was observed upon adsorption of thiophene with the order of magnitude of 0.045 Å.
- In Cu(I)Y, Ag(I)Y, and Zn(II)Y, the S–C bond length was larger upon adsorption than in the gas phase, by around 0.025Å, 0.016Å, and 0.018Å, respectively.
- In HY, LiY, NaY, KY, CsY, Cu(II)Y, DAY, and D-LAS, the S–C bond lengths were roughly similar in the gas phase and upon adsorption.

Except for EX-LAS, no significant difference was observed in the S-C bond length, between the gas phase and upon adsorption (no more than 0.03 Å), which ensures that dissociation of

thiophene cannot occur after adsorption. This means that in terms of regenerability, all studied formulations could be safely used for the adsorption of thiophene, except EX-LAS.

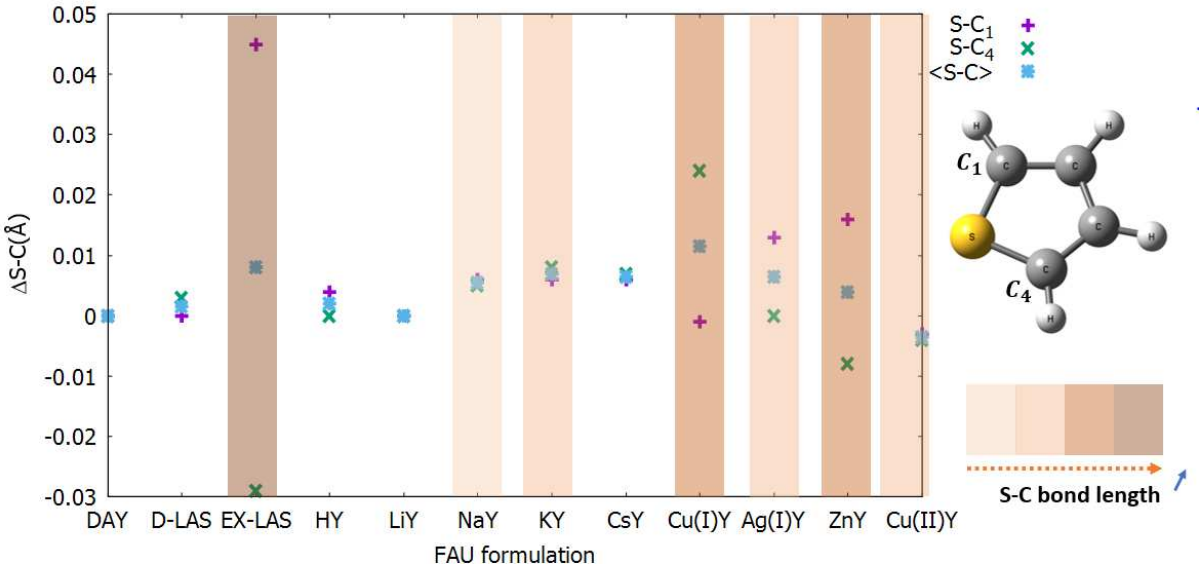

Fig. 3. S-C bond length of thiophene in gas phase and upon adsorption.

4. Conclusions

In the context of the deep desulfurization of transport fuels, our work aimed at identifying suitable faujasite (FAU) Y formulations for the selective adsorption of thiophene in the presence of benzene. Using periodic, vdW-corrected DFT calculations, we systematically studied the interactions of benzene and thiophene in DAY, FAU containing either Defect Lewis acid sites (D-LAS) or Extra framework Lewis acid sites (EX-LAS), and MY where M = H, Li, Na, K, Cs, Cu(I), Cu(II), Ag(I), and Zn(II).

Our main results can be summarized as follows:

(1) Benzene is adsorbed in any FAU formulation through π-interactions, respectively represented by π-staking of the aromatic ring on 6MR in DAY, by the interaction of 2

protons with the aromatic ring in HY, by M-aromatic ring interactions in MY (M = Li, Na, K, Cs, Cu(I), Cu(II), Ag(I), and Zn(II)), by Al-aromatic ring interactions in EX-LAS, and by π-staking of the aromatic ring on the 6MR containing the negative charge excess in D-LAS.

(2) The affinity of zeolites towards benzene decreases in the following order: bearing-EX-LAS FAU > Cu(I)Y > Zn(II)Y ≈ Ag (I)Y > bearing-D-LAS FAU ≈ CsY > NaY > HY > KY > LiY ≈ Cu(II)Y > DAY.

(3) Thiophene also adsorbed through its aromatic ring in the various sorbents. However, the presence of a sulfur atom in its aromatic ring leads to a behavior which is different from benzene.

(4) The affinity of thiophene for zeolites decreases in the following order: EX-LAS > Cu(I)Y > Zn(II)Y > D-LAS ≈ Ag(I)Y > CsY > HY.

Overall, bearing-LAS FAU (D-LAS, and EX-LAS), Cu(I)Y, Cu(II)Y, Zn(II)Y, CsY, and HY present a higher affinity for thiophene than for benzene. In particular, thiophene is more adsorbed on D-LAS than benzene by 17.7 kJ/mol, suggesting an outstanding trapping performance for D-LAS towards thiophene. In terms of regenerability, we have found that all of the formulations can be used safely except EX-LAS. In conclusion, we recommend the incorporation of defect Lewis acid sites in Y formulations to obtain a good compromise between high adsorption selectivity for thiophene in the presence of benzene, and limited C-S bond activation. Alternatively Zn(II)Y and Cu(II)Y could be tested experimentally for the ADS technology.

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GRAPHICAL ABSTRACT