A quantum chemical study for exploring the inhibitory effect of nitrogen containing species on the adsorption of polynuclear aromatic hydrocarbons over a Brønsted acid site

C M Celis-Cornejo1, M M Garnica Mantilla1, V G Baldovino-Medrano1 and G E Ramírez-Caballero1
1 Universidad Industrial de Santander, Bucaramanga, Colombia.

E-mail: ransereg@hotmail.com ; gusramca@uis.edu.co

Abstract. The analysis of the inhibitory effect of nitrogenated compounds on the hydproprocessing and hydropurification of oil derived fuels is important to produce cleaner fuels. In this work, density functional theory calculations were performed to investigate the effect of the nitrogen containing molecules on the adsorption of Polynuclear Aromatic Hydrocarbons (PAHs). Mordenite was chosen as a zeolitic structure for simulating a Brønsted acid site. The character of the acid site was confirmed by both a vibrational frequency calculation and a Bader charge analysis. From the adsorption calculations, it was found that the adsorption energy of PAHs increases with the number of aromatic rings in the structure. Also, the nitrogen containing species possibly inhibit more extensively two and three rings PAHs because of their lower adsorption energies. Finally, it was observed that the nitrogen species tend to drag the proton from the mordenite acid site. This explains the inhibitory effect in the adsorption of PAHs and contributes to understanding the dynamics of hydrocarbon hydroprocessing in refineries.

1. Introduction
Hydrocracking is key for transforming heavy oil feedstocks into desired liquid fractions such as gasolines and diesel. The heavier the fraction, the higher the concentration of heteroatoms [1]. Hydrocracking is usually preceded by hydrotreating in which sulfur, nitrogen and metal heteroatoms are removed [2]. After hydrotreating some refractory heteroatom species remain, nonetheless.

A previous study on the characterization of a Vacuum Gas Oil (VGO) and of its hydrotreated product (HDT-VGO) by Electrospray Ionization Fourier Transform Ion Cyclotron Mass Spectrometry (ESI FT-ICR-MS) showed that the most abundant nitrogen containing species in this VGO have a N₁ stoichiometry containing one nitrogen atom in their structure [3]. Furthermore, this study also showed that basic nitrogen species mostly comprise pyridine type structures such as quinolines and benzoquinolines in addition to non-basic nitrogen species which consist mainly on pyrrolic type structures such as carbazoles and benzo carbazoles [4]. Between these two nitrogenated families, the basic species are easier to remove during hydrotreatment as compared to the non-basic ones [3].

The effect of basic nitrogen molecules on the catalytic performance of hydrotreating materials has been copiously studied. Dufresne et al. [5] reported that it is necessary to increase 100°C the reactor temperature in order to level off the conversion in the reactor at 6.1kPa when increasing ammonia partial pressure. Molecules of this nature interact strongly with both Bronsted and Lewis acid sites. Korre et al. [6] found that the adsorption constants for ammonia on catalysts acid sites are two orders
of magnitude higher than those calculated for the hydrocracking of Polyaromatic Aromatic Hydrocarbons (PAHs). Sau et al. [7] established that concentrations of pyridine as low as 10ppm have a detrimental effect on hydrocracking [7]. Concerning the effect of non-basic nitrogen species on hydrocracking catalysts, the topic remains basically unexplored under the common assumption that only the effects of basic nitrogen species on hydrocracking are relevant [8]. However, Kobayashi et al. [9] reported a strong effect of non-basic carbazole over the activity and selectivity of hydrocracking catalysts even when the concentration of this molecule was not higher than 20ppm.

Phenanthrene and naphthalene are model molecules for heavy feedstocks. The hydrocracking of phenanthrene has thus been studied over Pt [10], FeW [11], NiW [6] and NiMo [12] based catalysts as well as over catalytic supports such as $\begin{array}{c}{\text{Al}}_{2}\text{O}_{3}\end{array}$ [12], HY and HZMS-5 zeolites [10], MCM-41 [10], and Al-SBA-15 [11]. In particular, studies over NiMo/HY catalysts have shown that phenanthrene hydrocracking is preceded by partial hydrogenation to intermediates such as: 1,2,3,4-Tetrahydrophenantrhene, 9,10-Dihydrophenantrhene and 1,2,3,4,5,6,7,8-Octahydrophenantrhene over the hydrogenating metal sites of the catalyst [6]. It is only after these reactions that isomerization, ring opening and dealkylation steps proceed over the supports Lewis and Brønsted acid sites. Figure 1 shows the hydroconversion route for the 1,2,3,4-Tetrahydrophenantrhene into naphthalene as under the above considerations.

Up to this point, the above discussion points out the importance of understanding what would be the inhibitory effect of non-basic nitrogenated molecules on the adsorption and reactivity of PAHs such as phenanthrene. Such understanding is important for perfecting kinetic modeling of the hydroconversion of heavy feedstocks. Consequently, we decided to make a first approach to the problem by performing Density Functional Theory (DFT) calculations for the adsorption of partial hydrogenated polynuclear hydrocarbons and of basic quinoline and non-basic carbazole over a model Brønsted acid site within a mordenite type zeolitic structure which is commonly used in hydrocracking.

2. Molecular simulation

In this section, the procedure for modeling the catalyst surface and the adsorption of the studied molecules are presented.

2.1. Mordenite structure

Mordenite has a unit cell containing 144 atoms. In comparison, faujasite and ZSM-5 [10] zeolites, also commonly used in hydrotreatment, contain 600 and 280 atoms, respectively. Therefore, calculations on mordenite have lower computational cost. Natural mordenite has the chemical formula: Na$_{4}$Si$_{18}$Al$_{18}$O$_{56}$•24H$_{2}$O, an orthorhombic morphology, a Cmcm space group, and crystallography unit cell parameters $a=18.052-18.168\text{Å}$, $b=20.404-20.527\text{Å}$ and $c=7.501-7.537\text{Å}$. Mordenite is a one-dimensional pore zeolite with ring sizes of 12, 8, 5 and 4-membered rings. The bulk mordenite CIF
file was taken from the Database of Zeolite Structures [13]. Initial unit cell parameters were $a=18.256\,\text{Å}$, $b=20.534\,\text{Å}$, and $c=7.542\,\text{Å}$. For the sake of convenience, the adsorption of the selected compounds was simulated over the 12-membered ring which has a cross section between 12.16Å and 11.25Å. Figure 2 shows the aforementioned physicochemical properties. After estimating the simulation parameters, a surface was created adding a vacuum space of 15Å over the [001] plane in order to expose the 12-membered ring. Terminal oxygen atoms were completed with hydrogen atoms. Following this procedure, we obtained a structure with 193 atoms.

2.2. Method
Calculations were carried out with the Vienna Ab-Initio Simulation Package (VASP) considering periodic boundary conditions. The Perdew–Burke–Ernzerhof exchange correlation functional (PBE) was considered in all cases. All of the simulation parameters were first estimated for the bulk mordenite system with smearing 0 and sigma parameter of 0.05. The energy cut off was also estimated initially at 1.3 times of the pseudopotential ENMAX value. A 400eV was chosen after a convergence study. A Γ-point Brillouin-zone sampling was considered due to the large size of the unit cell.

2.3. Acid site simulation
Commercial mordenite usually has Si/Al ratios ranging from 6 to 10 while some commercial Y zeolites have a Si/Al ratio from 5 to 37. For adding a Brønsted acid site to the zeolitic structure, the isomorphic substitution of one silicon atom by one aluminum atom was made in a structure with a Si/Al ratio of 47 (Figure 3). Such low Si/Al ratio is considered herein as representative of a very dealuminated acid support possessing an intermediate acidity such as those commonly used for hydrocracking. A vibrational frequency calculation was carried out to confirm the acid character of the simulated site. A Bader Topological Analysis was also performed using the algorithm developed by Henkelman and coworkers [14] for obtaining the accumulated charge of the atoms in the system and in order to estimate the electronic charge of the modeled acid site.

2.4. Adsorption of PAHs and nitrogenates
As discussed before, partial hydrogenation of the PAHs over the metallic active sites of the catalysts is a prerequisite for isomerization, ring opening, and dealkylation reactions. Therefore, only the adsorption of partially hydrogenated hydrocarbons such as 1,2,3,4-tetrahydronaphthalene, 1,2,3,4-tetrahydrophenanthrene, and 1,2,3,4-tetrahydrocrysene, 1,2,3,4-tetrahydrocarbazole, and quinoline and carbazole, over the model acid site were considered.
Each adsorbate was firstly optimized in a 25Å vacuum cube cell for avoiding interactions between the periodic images hence obtaining the energy of the isolated molecules \((E_m)\). Subsequently, the adsorption energy \((\Delta H_{ads})\) was calculated with the following Equation 1:

\[
\Delta H_{ads} = E_{m-zeo} - (E_m + E_{zeo})
\]

Where, \(E_{zeo}\) and \(E_{m-zeo}\) represent the mordenite catalytic surface and the mordenite-adsorbate complex energies, respectively.

Partially hydrogenated PAHs were adsorbed by the C’ carbon (see, Figure 4(a)), carbazol, its partially hydrogenated product, and quinoline were adsorbed by the N’ nitrogen (see Figure 4(b) and 4(c)). The choice of the latter was based on the fact that nitrogen has in these molecules a basic electron pair. Initial configurations were set at 1.1Å for each interaction considered. All of the calculations were relaxed without restrictions until all adsorbates reached an equilibrium distance from the acid site.

![Figure 4. Adsorption orientations: (a) 1,2,3,4-tetrahydronaphthalene, (b) 1,2,3,4-tetrahydrocarbazole, and (c) quinoline.](image)

3. Results and discussion

3.1. Catalyst surface and acid site
The parameters of the unit cell obtained after mordenite optimization were \(a=18.094\AA\), \(b=20.516\AA\), and \(c=7.524\AA\). From the stretching frequency calculations for the OH adjacent to the aluminum atom, a frequency of 3603.9cm\(^{-1}\) was obtained. This value very close to that reported by IR studies of Brønsted acid sites (3608cm\(^{-1}\)) [15]. The Bader charge analysis yielded a total charge of 896; this value corresponds to the external electrons considered by the Effective Core Potential. The accumulated charge for the hydrogen attached to the oxygen adjacent to the aluminum atom is about +0.75. This value is higher than that for terminal silanol groups that average +0.64. These results confirm the acid character of the simulated Brønsted acid site.

3.2. Adsorption of PAHs and nitrogen containing molecules
Table 1 shows that the adsorption energy for carbazole is higher than that of its partially hydrogenated product. Similar experimental [6] and theoretical [16] results have been reported. Now, the adsorption energy calculated for 1,2,3,4-tetrahydrocarbazole is higher than that for 1,2,3,4-tetrahydrophenanthrene as well as for 1,2,3,4-tetrahydronaphthalene. Hence suggesting a possible inhibitory effect of this nitrogen-containing molecule over the adsorption of species with three or two rings. On the other hand, 1,2,3,4-tetrahydrocrysene had a higher adsorption energy whereby it could be less inhibited by the presence of non-basic nitrogen containing species. The calculated trend for the adsorption energies for PAHs increases as long as aromatic rings are added to the structure, therefore
four ring PAHs displayed the highest adsorption energy. Thermochemical experiments for the hydrocracking of phenanthrene evidence that the equilibrium constant for 1,2,3,4-tetrahydrophenanthrene is higher than the one calculated for 1,2,3,4-tetrahydronaphthalene [6]. Therefore, our results agree well reported experiments. Finally, the quinoline adsorption energy was highest as in agreement with a strong interaction between its basic nitrogen heteroatom and the model Brønsted acid site.

Table 1. Adsorption energies calculated from Equation 1.

| Molecule                        | $\Delta H_{\text{ads}}$ (kJ/mol) |
|--------------------------------|----------------------------------|
| Carbazole                       | -486.77                          |
| 1,2,3,4-Tetrahydrocarbazole     | -481.53                          |
| Quinoline                       | -570.63                          |
| 1,2,3,4-Tetrahydronaphthalene   | -382.93                          |
| 1,2,3,4-Tetrahydrophenanthrene  | -414.93                          |
| 1,2,3,4-Tetrahydrocrysene       | -457.29                          |

Equilibrium distances calculated for the interactive atoms after relaxation are shown in Table 2. For PAHs, equilibrium distances were reached at 2.23, 2.15 and 2.07Å for 1,2,3,4-tetrahydronaphthalene, 1,2,3,4-tetrahydrophenanthrene, and 1,2,3,4-tetrahydrocrysene, respectively. Calculations show the displacement of all of the molecular structure due to a repulsive force until reaching an optimum distance. The herein obtained equilibrium distances are in good agreement with other theoretical works using the General Gradient Approximation (GGA) [17]. García-Serrano et al. [17] calculated distances of 2.16 and 2.20Å for the carbon-proton interactions. It should be noticed that the proton remains at the same initial position. For both non-basic nitrogenates, similar equilibrium distances were estimated but with a displacement of the proton. The latter is clearly attracted by the nitrogen heteroatom. Equilibrium distances for quinoline also show such an effect but with the proton closer to the nitrogen heteroatom and at a distance of 1.06Å which is almost the same as that for a N-H bond. This suggests that the inhibition occurs not only because the distances are shorter between nitrogen (N') and the proton (H+) but also because nitrogen draws the proton out of the mordenite structure. These trends agree with the known stronger inhibitory effect of basic nitrogen during hydrocraking reactions.

Table 2. Equilibrium distances for the interactive atoms after geometry optimization for all of the adsorbates.

| Molecule                        | Interaction | Distance (Å) |
|--------------------------------|-------------|--------------|
| Carbazole                       | N'---H+     | 1.13         |
|                                | H+---O      | 1.45         |
| 1,2,3,4-Tetrahydrocarbazole     | N'---H+     | 1.12         |
|                                | H+---O      | 1.45         |
| Quinoline                       | N'---H+     | 1.06         |
|                                | H+---O      | 1.51         |
| 1,2,3,4-Tetrahydronaphthalene   | C'---H+     | 2.20         |
|                                | H+---O      | 0.99         |
| 1,2,3,4-Tetrahydrophenanthrene  | C'---H+     | 2.14         |
|                                | H+---O      | 0.99         |
| 1,2,3,4-Tetrahydrocrysene       | C'---H+     | 2.09         |
|                                | H+---O      | 0.99         |
Finally, a Bader charge analysis of the complex quinoline-mordenite at the equilibrium distance shows that the charge of the proton is +0.51 while that of the neighboring oxygen shifts from -1.61 to -1.52. In the meantime, the charge for the nitrogen heteroatom shifts from -1.15 to -1.26. Consequently, a strong interaction between the proton moieties and the basic nitrogen of quinoline is well evidenced.

4. Conclusions
This work is a first theoretical approach to revealing the effect of non-basic nitrogenates on the hydrocracking of heavy oil fractions. Particularly, adsorption of non-basic and basic nitrogenated molecules such as carbazole, 1,2,3,4-tetrahydrocarbazole and quinolone, over a single Brønsted acid site, located at the surface of a mordenite structure was simulated. Calculations showed that the increase in the number of aromatic rings of the molecules leads to higher adsorption energies ($\Delta H_{ads}$). Nonetheless, the adsorption energy for the non-basic nitrogen species shows a possible inhibitory effect due to competition for the acid site with PAHs mainly with 2 and 3 rings. The shift observed in the position of the proton locating this closer to the nitrogenated adsorbate than to the mordenite evidences the inhibitory effect of nitrogenated compounds for the adsorption of PAHs in Brønsted acid sites.

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Corrigendum: A quantum chemical study for exploring the inhibitory effect of nitrogen containing species on the adsorption of polynuclear aromatic hydrocarbons over a Brønsted acid site

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C M Celis-Cornejo¹, M M Garnica Mantilla¹, V G Baldovino-Medrano¹ and G E Ramírez-Caballero¹

¹Universidad Industrial de Santander, Bucaramanga, Colombia.
E-mail: ransereg@hotmail.com; gusramca@uis.edu.co

The following list provides a description of the changes we made to the original publication that is available online, considering that the trend and the overall conclusions are the same.

Page 4:
In the third paragraph, the following text appears:
“All of the calculations were relaxed without restrictions until all adsorbates reached an equilibrium distance from the acid site.”
This should read:
“All of the calculations were relaxed considering Van de Waals interactions, until all adsorbates reached an equilibrium distance from the acid site.”

Page 4:
In the fifth paragraph, the following text appears:
“On the other hand, 1,2,3,4-tetrahydrocrysene had a higher adsorption energy whereby it could be less inhibited by the presence of non-basic nitrogen containing species.”
This should read:
“The energy for the 1,2,3,4-tetrahydrocrysene is similar to that obtained for the phenanthrene, this trend was also observed for adsorption of three membered and four membered PAHs over a NiMoS surface [16].”

Page 5:
In Table 1, the values of energy were compared with a calculation using a different potential, and it must be always the same, so we corrected this error and it should be read as follows:

| Molecule                        | $\Delta H_{ads}$ (kJ/mol) |
|---------------------------------|---------------------------|
| Carbazole                       | -116.58                   |
| 1,2,3,4-Tetrahydrocarbazole     | -99.4                     |
| Quinoline                       | -150.77                   |
| 1,2,3,4-Tetrahydronaphthalene   | -71.43                    |
| 1,2,3,4-Tetrahydrophenanthrene  | -78.57                    |
| 1,2,3,4-Tetrahydrocrysene       | -78.38                    |