



Adsorption structures of heterocyclic nitrogen compounds over Cu(I)Y zeolite: A first principle study on mechanism of the denitrogenation and the effect of nitrogen compounds on adsorptive desulfurization

Dan Liu*, Jianzhou Gui, Zhaolin Sun

College of Chemistry and Materials Science, Liaoning Shihua University, Dandong Road West 1#, Fushun 113001, Liaoning, PR China

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ABSTRACT

The adsorption configurations of quinoline, acridine, indole and carbazole over Cu(I)Y zeolite were studied by the density functional theory (DFT) method. The η^2 adsorption mode has been found to be energetically preferred for neutral nitrogen compounds, i.e. indole and carbazole; while for basic ones, quinoline and acridine, the $\eta^1\text{N}$ adsorption mode is the most preferential one, implying that in the competitive adsorption aromatics show a strong preference over neutral nitrogen compounds than over basic ones. The adsorption energies of the adsorbate over Cu(I)Y zeolite decrease as follows: basic heterocyclic nitrogen compounds > neutral heterocyclic nitrogen compounds > thiophenic compounds, suggesting that deep denitrogenation and desulfurization could be carried out simultaneously over Cu(I)Y zeolite under ambient temperature, while for Cu(I)Y zeolite the adsorption of nitrogen compounds is preferable to that of sulfur compounds, and good selectivity will be shown for the basic nitrogen compounds during denitrogenation. Meanwhile, when the adsorbent is used for selective deep desulfurization, the presence of nitrogen compounds can greatly retard sulfur removal.

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1. Introduction

Deep denitrogenation and desulfurization of fuels have drawn extensive attention worldwide due to the increasingly stringent regulations for environment and fuel specifications in many countries [1–4]. Conventional hydrotreating methods have been effective for the easy-to-remove sulfur and nitrogen compounds, while less competent for removing heterocyclic sulfur or nitrogen compounds (such as benzothiophenes (BTs), dibenzothiophenes (DBTs), indoles, quinolines, carbazoles, acridines, etc.) which are abundant especially in diesel. Although the nitrogen concentration in diesel fuel is usually much lower than the sulfur concentration, the nitrogen compounds coexisting in middle-distillate oil can inhibit the ultra-deep HDS. Meanwhile, the removal of such nitrogen compounds from the middle-distillate oil can improve significantly the ultra-deep HDS performance [5–9]. In addition, nitrogen compounds in the fuel and NH_3 produced during hydrocarbon reforming process are also poisons to the catalysts. Now it is necessary to develop new approaches to ultra-deep desulfurization and denitrogenation for diesel fuel.

Selective adsorption methods are very promising for removing the refractory sulfur or nitrogen compounds at ambient temperature and pressure, which may finally lead to major advances in petroleum refining [10–13]. Adsorbent Cu(I)Y has been reported to be capable of both deep desulfurization and denitrogenation with high selectivity and high capacity by Yang and his co-workers [14–28]. The interactions of adsorbent and heterocyclic sulfur or nitrogen compounds were owing to π -complexation.

In our previous studies the interaction of the adsorbent Cu(I)Y and thiophenic sulfur compounds has been investigated systematically with first principle calculations and both π -complexation and direct metal–sulfur interaction have been found [29,30]. It is interesting that the η^2 adsorption mode through the C=C bond of the thiophenic ring has been found to be energetically preferred for the BTs, abundant in gasoline, while for the DBTs, mainly available in diesel fuel, the $\eta^1\text{S}$ adsorption mode is the most preferential one, implying that in the competitive adsorption on Cu(I)Y aromatics show a stronger preference over S-compounds in gasoline than in diesel fuel.

Little has been reported on the possible adsorption configurations of the heterocyclic nitrogen compounds in transportation fuels over adsorbents by either of theoretical and experimental methods. The chief aim of the present work is to investigate the possible adsorption configurations of indole, quinoline, carbazole and acridine on the Cu(I)Y adsorbent using DFT method to get a

* Corresponding author. Tel.: +86 413 6865161.

E-mail addresses: danliu_939@hotmail.com, ldan2000@163.com (D. Liu).

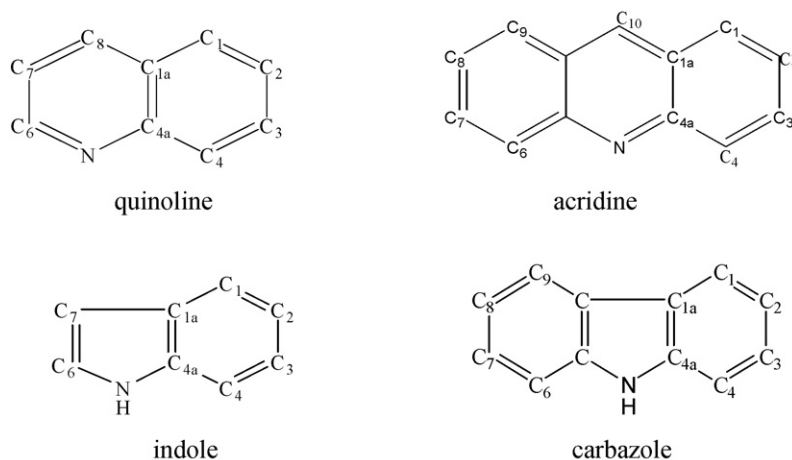


Fig. 1. Atom labeling in four heterocyclic nitrogen compounds.

better understanding of the adsorption mechanisms in deep denitrogenation of gasoline and diesel fuels and the effect of nitrogen compounds on adsorptive desulfurization.

2. Calculation details

All calculations were performed by applying the generalized gradient-corrected density functional theory (DFT) using the DMol³ module in Materials Studios 3.1 package of Accelrys. In order to make a good comparison with the adsorption of S-compounds in previous studies [29,30], the same calculation parameters have been employed for the adsorption of N-compounds over Cu(I)Y zeolite, e.g. PBE exchange correlation function, double-numeric quality basis set with polarization functions (DNP), spin-restricted and density functional semicore pseudopotentials (DSPP), etc. A thermal smearing of 0.002 Hartree and an orbital cut-off of 4 Å was used to improve the computational performance. All SCF tolerances were set to fine, i.e. the tolerance of energy, gradient and displacement being converged to 1.0E–5 ha, 0.002 ha/Å and 0.005 Å, respectively.

Experimental studies showed that SiteII, sitting in the center of the six-membered rings that connect the sodalite cage with the supercage, are the preferential adsorption site for cyclic N- or S-compounds. Thus, a six-membered-ring cluster, proven to be valid in our previous work [29,30], was chosen as the Cu(I)Y zeolite cluster in this study. Prior to the adsorption calculations, the structures of the heterocyclic nitrogen compounds are fully optimized, while for the zeolite cluster, partial geometry optimization was applied. For the simulations of all the adsorption configurations of the systems, the whole heterocyclic nitrogen compounds were allowed to relax, whereas for the Cu(I)Y cluster, only 13 atoms (including cuprous atom) of the six-membered ring in the cluster were allowed to relax and the other atoms were fixed. The population analysis was also performed for all the structures.

The adsorption energy was computed by using the expression

$$\Delta E_{\text{ads}} = E_{\text{adsorbent-adsorbate}} - E_{\text{adsorbent}} - E_{\text{adsorbate}}$$

where $E_{\text{adsorbent-adsorbate}}$ is the total energy of the optimized adsorbent/adsorbate system, $E_{\text{adsorbent}}$ is the total energy of the partially optimized Cu(I)Y clusters and $E_{\text{adsorbate}}$ the total energy of the free adsorbate. The negative ΔE_{ads} values indicate that adsorption is an exothermic process, and a more negative value corresponds to a stronger adsorption.

3. Results and discussion

3.1. Geometry optimization of heterocyclic nitrogen compounds

Two classes of heterocyclic nitrogen compounds exist in the crude oils, including six-membered pyridines (basic) and five-membered pyrroles (neutral). Some typical compounds (quinoline, acridine, indole and carbazole) and their atom labeling are shown in Fig. 1. The structural parameters and electronic properties of quinoline, acridine, indole and carbazole, obtained by the optimization using the DFT method, are listed in Table 1.

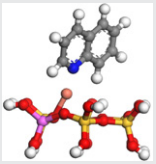
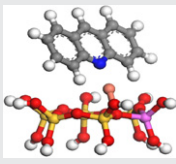
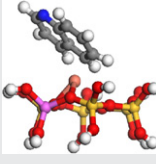
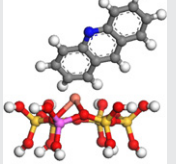
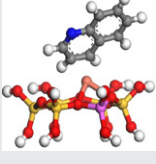
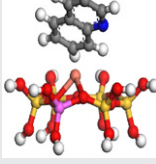
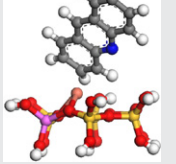
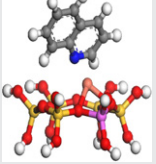
As for the basic heterocyclic nitrogen compounds containing six-membered pyridine ring, the lone pair of N atom is not part of the aromatic system and extends in the plane of the ring, so this lone pair is responsible for its basicity. While in the neutral ones containing five-membered pyrrole ring, the lone pair of the nitrogen atom is delocalized and contributes to the aromatic π electron system. That is the reason why charge on the N atoms is more negative on the basic nitrogen-containing compound than neutral one. The compounds of acridine and carbazole have a higher symmetry of C_{2v} and show a smaller dipole moment than the corresponding quinoline and indole, respectively.

In all the four compounds, all C–C bonds are involved in a π conjugated system, all double bonds tend to lengthen, and single bonds tend to shorten, the main difference between the basic and neutral ones is whether the lone pair of nitrogen atom is involved in the conjugated system. The highest bond order of C–C bonds in the molecules increases in the order of carbazole < quinoline < acridine < indole, which is involved in the phenyl ring for the first three ones and in the pyrrole ring for the indole.

Table 1
Structural and electronic parameters of four heterocyclic nitrogen compounds

	Quinoline	Acridine	Indole	Carbazole
Molecular properties	Basic	Basic	Neutral	Neutral
C–C with highest Mayer bond order	C ₁ –C ₂	C ₁ –C ₂	C ₆ –C ₇	C ₁ –C ₂
Its Mayer bond order	1.5036	1.5383	1.5652	1.4512
Its bond length	1.380	1.375	1.375	1.394
Mulliken charge (on N atom)	–0.332	–0.346	–0.357	–0.400
Hirshfeld charge (on N atom)	–0.161	–0.161	–0.067	–0.074
ESP charge (on N atom)	–0.699	–0.720	–0.449	–0.705
Dipole moment, <i>D</i>	2.1038	1.9243	1.8442	1.6665
Symmetry	C _s	C _{2v}	C _s	C _{2v}

Table 2
Possible adsorption configurations of quinoline and acridine on Cu(I)Y zeolite and corresponding adsorption modes and energies

Quinoline adsorption configurations	Adsorption modes	ΔE_{ads} (kJ/mol)	Acridine adsorption configurations	Adsorption modes	ΔE_{ads} (kJ/mol)
	$\eta^1\text{N}$	–130.9		$\eta^1\text{N}$	–126.9
	$\eta^2(\text{C}_1\text{-C}_2)$	–108.1		$\eta^2(\text{C}_1\text{-C}_2)$	–102.7
	$\eta^2(\text{C}_7\text{-C}_8)$	–102.5	–	–	–
	$\eta^2(\text{C}_3\text{-C}_4)$	–100.2		$\eta^2(\text{C}_3\text{-C}_4)$	–96.8
	$\eta^2(\text{C}_6\text{-N})$	–89.2	–	–	–

Note 1:  is Cu atom;  is N atom.

3.2. Adsorption configurations calculations

By examining the possible configurations, several major binding modes of quinoline, acridine, indole and carbazole on the Cu(I)Y zeolite were defined as follows (see Tables 2 and 3):

- $\eta^1\text{N}$ adsorption mode through the direct metal–nitrogen interaction.
- η^2 adsorption modes through the conjugated double bond in the phenyl ring or in the pyridine or pyrrole ring, named η^2 (name of the particular double bond), respectively.

The above adsorption modes may have more than one configurations with these organonitrogen compounds orienting on the Cu(I)Y cluster, but the difference in the adsorption energies of different configurations for the same adsorption modes is insignificant.

3.2.1. Adsorption of basic heterocyclic nitrogen compounds

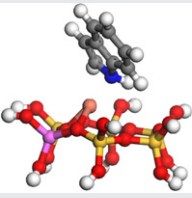
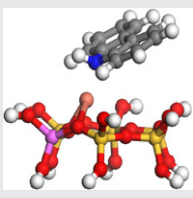
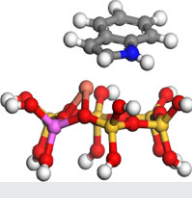
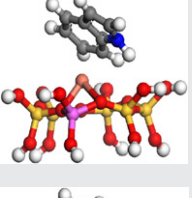
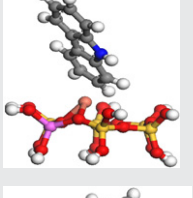
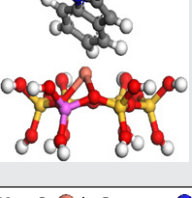
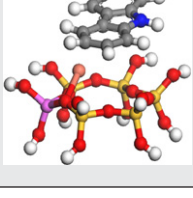
According to the interaction of organonitrogen and the Cu(I)Y adsorbent, there must be five and three possible adsorption configurations existing for quinoline and acridine adsorption, respectively. Table 2 lists the possible adsorption configurations of the two model nitrogen compounds and their corresponding adsorption energy. As for quinoline and acridine, the $\eta^1\text{N}$ adsorp-

tion mode, with adsorption energy of –130.9 and –126.9 kJ/mol, respectively, is the most energetically preferential one, and each $\eta^1\text{N}$ adsorption mode has a new chemical bond between Cu and N atoms formed, the bond length being 1.872 and 1.896 Å, respectively with its corresponding Mayer bond order 0.8011 and 0.7924. This means that the Cu–N bond shows more covalent and slight ionic characteristics. The slight difference in the adsorption energy demonstrated that little changes in electronic properties of N caused by the additional phenyl ring of acridine as compared with quinoline.

The most favourable adsorption mode for BT and DBT over the Cu(I)Y zeolite was demonstrated, in our previous study, to be the η^2 adsorption with an adsorption energy of –96.4 kJ/mol and $\eta^1\text{S}$ adsorption of –88.5 kJ/mol, respectively. Their adsorption energies are significantly lower than those of the corresponding basic heterocyclic nitrogen compounds quinoline and acridine, meaning during desulfurization the basic heterocyclic nitrogen compounds will be preferentially adsorbed over this adsorbent and will greatly affect the desulfurization. The adsorbent is a better one for basic nitrogen compounds than sulfur compounds.

In the η^2 adsorption modes of quinoline, the double bond which could be directly bonded to the Cu atom could be $\text{C}_1\text{-C}_2$, $\text{C}_7\text{-C}_8$, $\text{C}_3\text{-C}_4$ and $\text{C}_6\text{-N}$ with bond orders 1.5036, 1.5015, 1.4916 and 1.5777, respectively, the corresponding adsorption energy of each modes are –108.1, –102.5, –100.2 and –89.2 kJ/mol, while in the two η^2

Table 3
Possible adsorption configurations for indole and carbazole on Cu(I)Y adsorbent and corresponding adsorption modes and energies

Indole adsorption configurations	Adsorption modes	ΔE_{ads} (kJ/mol)	Carbazole adsorption configurations	Adsorption modes	ΔE_{ads} (kJ/mol)
	$\eta^1\text{N}$	-70.9		$\eta^1\text{N}$	-69.1
	$\eta^2(\text{C}_6\text{-C}_7)$	-112.9	-	-	-
	$\eta^2(\text{C}_3\text{-C}_4)$	-116.6		$\eta^2(\text{C}_3\text{-C}_4)$	-99.2
	$\eta^2(\text{C}_1\text{-C}_2)$	-104.5		$\eta^2(\text{C}_1\text{-C}_2)$	-95.1

Note 2: ● is Cu atom; ● is N atom.

adsorption modes of acridine, the bonded C–C bond in acridine molecule is C₁–C₂ and C₃–C₄ with a bond order of 1.5383 and 1.5280 each, and the corresponding adsorption energies are -102.7 and -96.8 kJ/mol, respectively. It can be seen from Table 2 that the strongest interactions between the adsorbate molecules and the Cu(I)Y cluster are through the C=C bond with the largest bond order, i.e. C₁–C₂; the bigger the bond order of the particular bond mentioned above (except C₆–N), the more negative adsorption energy of the adsorption configuration. While the adsorption configuration, in which the Cu atom is directly bonded to C₆–N, is the most unstable one. Compared with quinoline, a slight decrease in the adsorption energy of the same modes may also be caused by the additional phenyl ring of acridine.

3.2.2. Adsorption of neutral heterocyclic nitrogen compounds

Adsorption configurations and the corresponding adsorption energies calculated for all the different adsorption modes of indole and carbazole are compiled in Table 3.

For the adsorption of both indole and carbazole, the $\eta^1\text{N}$ adsorption is the most unstable adsorption mode with less negative adsorption energy. In this mode, the H atom bonded with the N atom in indole and carbazole are far away from the molecular plane and the distortion of the molecular plane may lead to the decrease in the adsorption energy.

The C–C bond with largest bond order in indole and carbazole is C₆–C₇ and C₃–C₄, respectively, while in the possible η^2 adsorption mode, $\eta^2(\text{C}_3\text{-C}_4)$ adsorption modes are the most preferred adsorption ones for both the two molecules over Cu(I)Y zeolite. It is interesting that the adsorption mode $\eta^2(\text{C}_3\text{-C}_4)$, as for indole

adsorption, is more favourable than $\eta^2(\text{C}_6\text{-C}_7)$. This is caused by the presence of the hydrogen bond in the $\eta^2(\text{C}_3\text{-C}_4)$ mode between the framework oxygen atom of Cu(I)Y cluster and the H atom of indole bonded to the N atom directly, leading to stronger adsorption interaction. The small cluster of Cu(I)Y zeolite is sufficient to show the local metal active site for the adsorption, since the adsorption site has been considered to be essentially local, while this cluster cannot describe properly the possibility of hydrogen bond between zeolite framework and neutral nitrogen compounds.

The most stable adsorption energies decrease in the order of basic heterocyclic nitrogen compounds > neutral heterocyclic nitrogen compounds > thiophenic compounds in diesel. So the adsorption of nitrogen compounds on Cu(I)Y zeolite is preferable to that of sulfur compounds, and higher selectivity of basic nitrogen compounds than neutral ones has been found. For basic and neutral heterocyclic nitrogen compounds, the most energetically preferable adsorption mode is $\eta^1\text{N}$ and η^2 , respectively. Therefore, during denitrogenation aromatics show a stronger preference over neutral compounds in the competitive adsorption than over basic ones.

4. Conclusions

From the possible adsorption structures of heterocyclic nitrogen compounds on Cu(I)Y zeolite determined by the DFT method, it can be concluded that the η^2 adsorption mode is energetically preferred for neutral compounds such as indole and carbazole, and the possible hydrogen bond should be taken into account as well; however, the $\eta^1\text{N}$ adsorption mode is the most stable one

for quinoline and acridine, the basic heterocyclic nitrogen compounds. It is suggested that in the competitive adsorption aromatics show a stronger preference over neutral nitrogen compounds than over basic ones. The adsorption energy of the adsorbate decreased as follows: basic heterocyclic nitrogen compounds > neutral heterocyclic nitrogen compounds > thiophenic compounds in diesel, suggesting that good selectivity will be shown for the basic nitrogen compounds than neutral ones during denitrogenation, while Cu(I)Y zeolite is a preferable adsorbent for nitrogen compounds rather than sulfur compounds when deep denitrogenation and desulfurization is carried out simultaneously over it under ambient temperature. While the adsorbent works for selective desulfurization, the presence of nitrogen compounds can greatly affect the results.

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