CO and NO desorption from N−bounded carbonaceous surface complexes: Density functional theory calculations

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CO and NO desorption from N-bounded carbonaceous surface complexes: density functional theory calculations

Shaobin Wang*

Department of Chemical Engineering, Curtin University of Technology, Perth, WA 6845, Australia

ABSTRACT: The reaction of N-bounded carbon with oxygen and subsequent desorption at molecular level was investigated using a density functional theory. The calculations show that the structure of surface N-containing carbon complexes will show different behaviour in CO and NO desorption after chemisorption of O_2. For the dissociative adsorption of O_2 on N-containing carbon surface, there is no significant difference in armchair and zigzag structure in terms of thermodynamics. However, the desorption of CO and NO from adsorbed complexes shows difference depending on the graphite structure. For zigzag structure, desorption of CO will be more favourable than NO, while for armchair CO and NO desorption will both be favourable. On the basis of the computation results, a reaction mechanism for N-bounded carbon combustion is proposed. © 2009 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: coal combustion; chemisorption; NO desorption; quantum chemical calculation

INTRODUCTION

The release of nitrogen oxides during coal combustion has a major environmental impact. The chemistry of the formation of nitrogen oxides during coal combustion is complex and many features are still not fully understood. In the past decades, significant progress has been made in understanding how the volatile nitrogen species in coal can be converted to N_2, NO, and N_2O by homogeneous reactions with oxygen in the gas phase while the mechanism of the conversion of the nitrogen remaining in the solid char after pyrolysis is less well understood. The experimental results on NO and N_2O formation vary widely with char type and experimental conditions while no exact mechanism and kinetic model have been established.[1,2]

In the last few years, some investigations using quantum chemical calculation have been conducted in understanding the adsorption process of NO or N_2O onto carbon for their reduction. Kyotani and Tomita simulated the chemisorption process of these gas molecules on zigzag and armchair edge sites of carbon by calculating the thermodynamics and the orbital bond data using an *ab initio* molecular orbital theory.[3] Later on, Zhu *et al*. introduced O_2 adsorption and investigated the opposite roles of O_2 in NO– and N_2O– carbon reactions.[4] Montoya *et al*.[5] investigated the reaction

of NO with char-bounded nitrogen during combustion using density function theory (DFT) method in order to elucidate mechanisms for N_2O evolution. They used a zigzag structure as char model and found that NO molecule reacted with char-N to release predominantly N_2 and CO to the gas phase. For the model char structures studied, the presence of adsorbed oxygen on the char-containing nitrogen enhances the reduction of the NO molecule to N_2, but N_2O can also be released as a minor nitrogen product. In the follow-up study, they investigated the desorption of NO from nitrogen-containing carbonaceous surfaces, a pyridine-N-oxide model, but found major discrepancies between theoretical and experimental activation energies for the NO desorption.[6]

Basically, a gas-phase oxygen molecule reacts with a surface nitrogen atom of the char to form stable nitrogen–oxygen complexes that can desorb NO. As stated above, the previous researches using quantum chemical calculation were concentrated on NO reduction in aspect of thermodynamics. However, no research has been reported in investigating the oxidation processes of N-bounded char with oxygen and its subsequent decomposition using quantum chemical calculation, whereas it is important to investigate the precursors of the surface functional groups. Therefore, it is necessary to conduct a more comprehensive study starting from the different electronic structures of armchair and zigzag edge sites, followed by both adsorption and desorption of nitrogen-containing gases on these different edge sites. The present study will present a study on O_2 adsorption

*Correspondence to: Shaobin Wang, Department of Chemical Engineering, Curtin University of Technology, Perth, WA 6845, Australia.
E-mail: shaobin.wang@curtin.edu.au

on N-bounded carbon and desorption by starting from the different manners of chemisorption of gases and the possible pathways for the subsequent gasification to understand the behaviour of CO and NO production.

COMPUTATIONAL DETAILS

Four different molecular char-nitrogen models with zigzag or armchair structure were proposed and are presented in Fig. 1. The Gaussian 98 package was used in this study.[7] The DFT B3LYP with the higher level model chemistry B3LYP/6-31G(d) is used to get accurate energy values. It is known that B3LYP produces fairly accurate bond energies and thermodynamic properties of reactions.[8] The unrestricted open-shell wave function was used in all open-shell cases. All the calculations include the following steps: geometric optimisation for optimising the molecular system to a minimum on the potential energy surface, single-point calculations, and frequency calculation. In addition, before optimising reactants, intermediates, and products for the ground state, we have performed single-point energy calculations using optimised geometries at a lower level of theory for estimating energies at different electronic states to determine the correct ground state. The heat of adsorption and desorption and Gibbs free energy were calculated based on the corrected thermal energy of the optimised products and reactants.

RESULTS AND DISCUSSION

Adsorption of O_2 on carbon surface

In general, O_2 can approach an electron-rich site of the carbon basal plane of graphite in two modes, side on and vertical. Kyotani *et al*.[9] studied the reaction of O_2
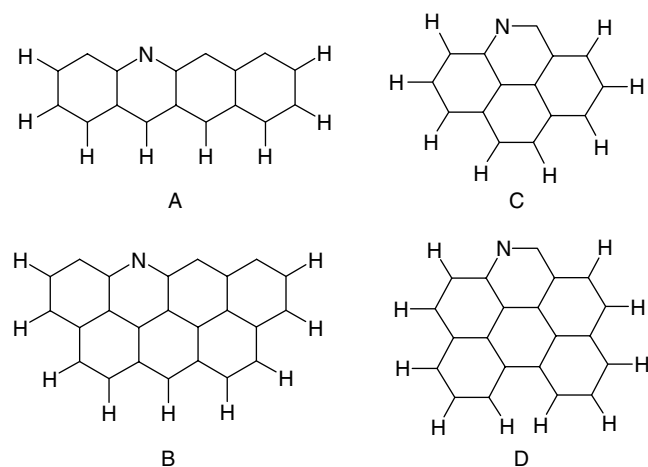
to the edge of a zigzag carbon structure using *ab initio* molecular orbital theory and found that the O_2 side-on adsorption mode is the most exothermic adsorption configuration. Therefore, the in-plane O_2 side-on approach was used to characterise the nature of carbon and nitrogen−oxygen complexes. In the previous investigation, it was also found that both the adsorbed O_2 tend to dissociate after chemisorption.[10,11] Figure 2 shows the dissociative chemi-adsoprtion species of nitrogen−oxygen groups. The changes of enthalpy (ΔH^0) and Gibbs free energy (ΔG^0) during the dissociative chemisorption are displayed in Table 1. Chemisorption of O_2 on pyridine-N-carbon surface in either armchair or zigzag structure is a strong exothermic reaction. Chemical structures of F and G will be more stable while the formation of E and H will have similar ΔH^0 and ΔG^0. It is suggested that graphite in either zigzag or armchair structure has the similar tendency toward oxygen chemisorption.

The bond length and atomic bond population are given in Table 2. For the zigzag structure, the C−N bond length adjacent to N−O is shorter than that of the C−C bond adjacent to C−O and the bond population is relatively higher. In addition, the N−O distance is longer than the C−O bond distance. These suggest that breakage of the two C−C bonds making the desorption of CO would be easier. While in case of
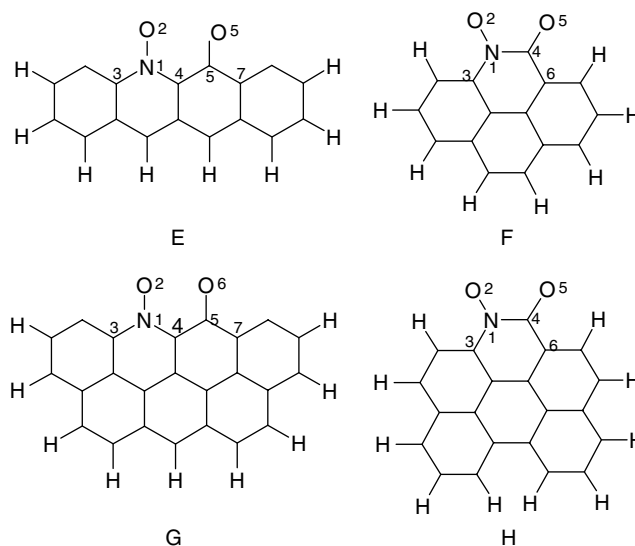
Figure 2. Models of O_2 dissociative chemi-adsorbed N-bounded complexes.

Table 1. ΔH^0 and ΔG^0 for oxygen chemisorption.

Model	ΔH^0 (kcal/mol)	ΔG^0 (kcal/mol)
E	−77.8	−66.3
F	−84.5	−72.9
G	−92.4	−80.5
H	−78.7	−67.0

Figure 1. Models for nitrogen-containing char.

Table 2. Bond length and atomic bond population.

Model	Bond	Length (Å)	Bond population
E	N(1)–O(2)	1.26	0.263
	N(1)–C(3)	1.42	0.214
	N(1)–C(4)	1.37	0.248
	C(4)–C(5)	1.49	0.205
	C(5)–O(6)	1.23	0.601
	C(5)–C(7)	1.49	0.233
F	N(1)–O(2)	1.27	0.171
	N(1)–C(3)	1.42	0.190
	N(1)–C(4)	1.46	0.073
	C(4)–O(5)	1.21	0.616
	C(4)–C(6)	1.46	0.214
G	N(1)–O(2)	1.26	0.267
	N(1)–C(3)	1.42	0.183
	N(1)–C(4)	1.37	0.230
	C(4)–C(5)	1.49	0.171
	C(5)–O(6)	1.22	0.615
	C(5)–C(7)	1.49	0.204
H	N(1)–O(2)	1.27	0.174
	N(1)–C(3)	1.40	0.196
	N(1)–C(4)	1.46	0.068
	C(4)–O(5)	1.22	0.612
	C(4)–C(6)	1.46	0.223

Figure 3. Structures of products formed after CO or NO desorption from model E.

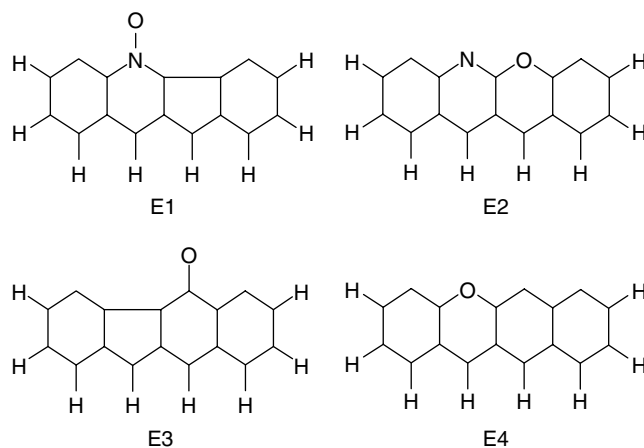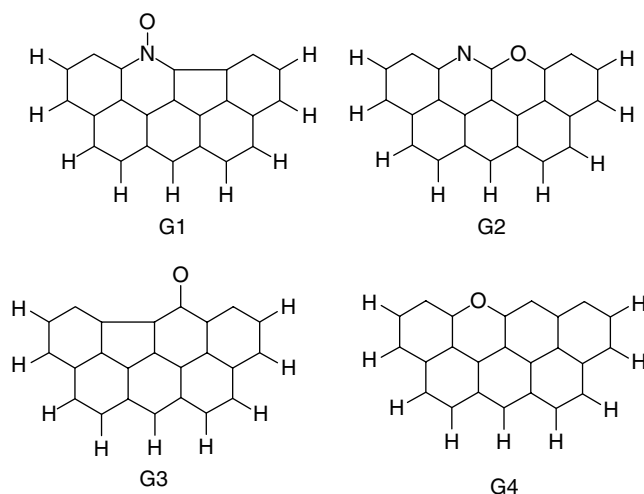**Figure 4.** Structures of products formed after CO or NO desorption from model G.

the armchair structure, the N–C(4) is much weaker with much smaller bond population. The C(3)–N bond length is shorter than that of C(4)–C(6), but the bond population of C(3)–N is weaker, which may imply that the desorption of CO or NO both can occur. Comparing the bond length of C–O and N–O, it is seen that C–O length is shorter and the bond population is higher.

Desorption of CO or NO from the zigzag structure

Figures 3 and 4 show the possible desorption products of CO or NO from the chemically structural models, E and G. Table 3 shows the changes of enthalpy (ΔH^0) and Gibbs free energy (ΔG^0) during the desorption. The desorption products of E2 and G2 present negative values of ΔH^0 and ΔG^0 while other three products of models E and G have positive values, suggesting that E2 and G2 are the most stable products. Comparing the products of CO and NO, it is also seen that ΔH^0 and ΔG^0 for CO desorption are lower than those of NO desorption, thus indicating that CO desorption is more favourable than NO desorption on zigzag structure.

Desorption of CO or NO from the armchair structure

Figures 5 and 6 show the possible desorption products of CO or NO from the chemically structural models,

Table 3. ΔH^0 and ΔG^0 for CO or NO desorption.

Model	ΔH^0 (kcal/mol)	ΔG^0 (kcal/mol)	Model	ΔH^0 (kcal/mol)	ΔG^0 (kcal/mol)
E1	9.1	2.2	G1	32.6	21.0
E2	−29.2	−40.5	G2	−27.7	−38.8
E3	27.4	15.1	G3	45.2	32.6
E4	68.1	56.0	G4	69.5	57.4

F and H and the changes of enthalpy (ΔH^0) and Gibbs free energy (ΔG^0) during the desorption are presented in Table 4. It is seen that ΔH^0 and ΔG^0 are much similar for desorption products, F2, and F5, which suggests that CO or NO desorption can occur for armchair model F. For all six products from model F, F3 presents the lowest ΔH^0 and ΔG^0. Similarly, H2
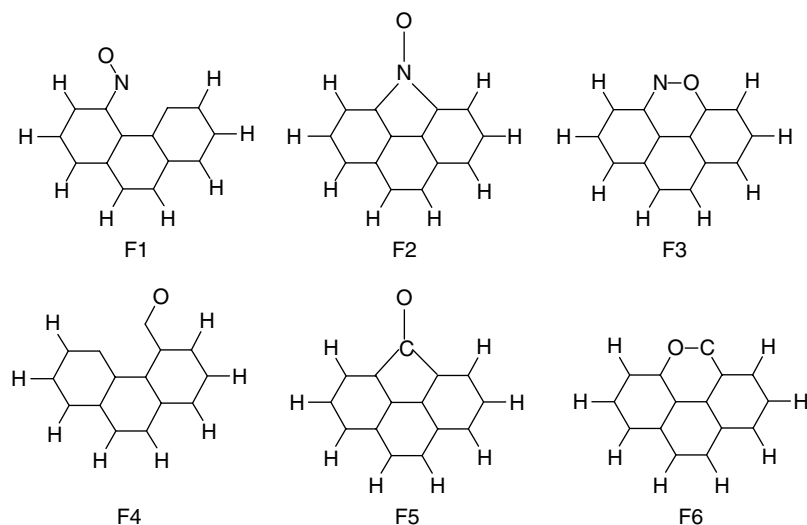
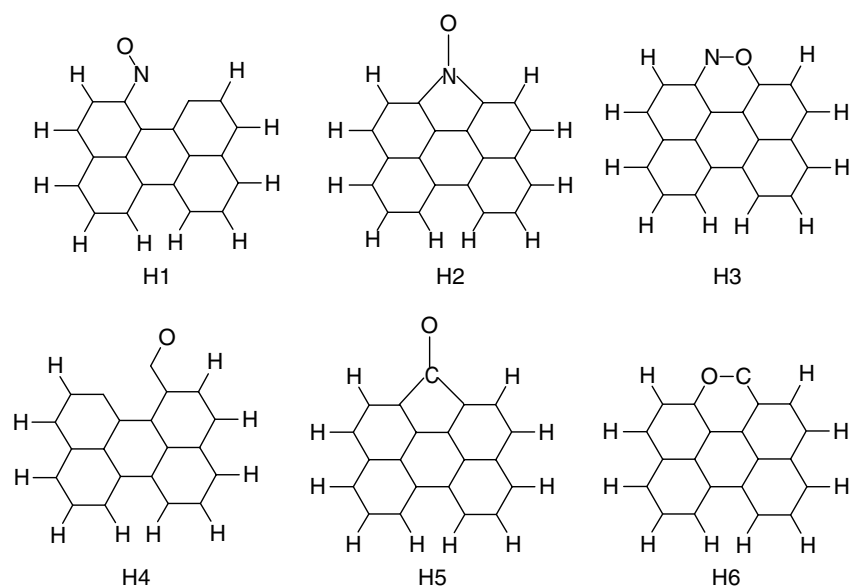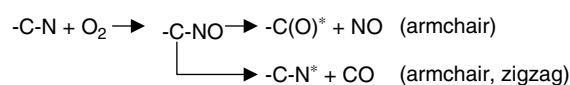**Figure 5.** Structures of products formed after CO or NO desorption from model F.

Figure 6. Structures of products formed after CO or NO desorption from model H.

Table 4. ΔH^0 and ΔG^0 for CO or NO desorption.

Model	ΔH^0 (kcal/ mol)	ΔG^0 (kcal/mol)	Model	ΔH^0 (kcal/mol)	ΔG^0 (kcal/ mol)
F1	95.6	81.5	H1	96.8	82.4
F2	31.5	19.7	H2	35.8	24.1
F3	26.2	14.5	H3	24.4	12.8
F4	109.1	94.3	H4	106.0	91.5
F5	29.2	17.3	H5	34.8	23.0
F6	95.1	82.6	H6	95.0	82.5

and H5 are also presenting low ΔH^0 and ΔG^0 and H3 gives the lowest values of ΔH^0 and ΔG^0. Thus, it is deduced that CO and NO desorption both will occur.

Therefore, a reaction mechanism for N-bounded carbon can be deduced based on the calculations for armchair and zigzag structure, which can be listed as follows:

$$-C\text{-}N + O_2 \rightarrow -C\text{-}NO \rightarrow -C(O)^* + NO \quad \text{(armchair)}$$
$$\rightarrow -C\text{-}N^* + CO \quad \text{(armchair, zigzag)}$$

In the experimental investigation, thermodynamic and kinetic parameters for the direct NO production channel have been difficult to obtain accurately because

some NO can be easily reduced *in situ* to form N_2. The rate of the direct NO production from char-N oxidation is typically assumed to be proportional to the rate of carbon oxidation from char in many single particles models.[6] Garcia *et al*. reported that the desorption activation energy of nitric oxide chemisorbed on carbon is a combination of two normal distribution functions, centred at energies around 150 and 190 kJ/mol which corresponds to the desorption of NO from organic structures as was previously determined by X-ray photoelectron spectroscopy (XPS), analysis at 100 °C,[12] while the activation energy for CO desorption obtained from temperature programmed desorption is in the range of 334–355 kJ/mol at high temperatures.[13] However, Montoya *et al*. investigated NO and CO desorption and obtained the transition state rate constant for the NO and CO desorption at different temperatures. The desorption rate constant for CO is slightly larger than the NO desorption rate constant. The difference in the rate constant becomes bigger as the temperature increases.[6] This is similar to the findings of this calculation that CO production would be more than NO.

CONCLUSION

Quantum chemical calculations indicate that zigzag and armchair N-bounded graphite shows strong dissociative chemisorption of oxygen. However, desorption of CO or NO from the adsorbed N-bounded carbon will behave differently depending on the zigzag and armchair structures. In terms of thermodynamic calculations, CO desorption from zigzag structure will be exothermic reaction and will be more favourable than NO desorption. For armchair carbon structure, ΔH^0 and ΔG^0 for CO

and NO desorption are quite similar and thus CO and NO desorption both will favourably occur.

REFERENCES

[1] I. Aarna, E.M. Suuberg. *Fuel,* **1997;** *76*(6), 475–491.
[2] Y.H. Li, G.Q. Lu, V. Rudolph. *Chem. Eng. Sci.,* **1998;** *53*(1), 1–26.
[3] T. Kyotani, A. Tomita. *J. Phys. Chem. B,* **1999;** *103*(17), 3434–3441.
[4] Z.H. Zhu, J. Finnerty, G.Q. Lu, R.T. Yang. *J. Phys. Chem. B,* **2001;** *105*(4), 821–830.
[5] A. Montoya, T.N. Truong, A.F. Sarofim. *J. Phys. Chem. A,* **2000;** *104*(36), 8409–8417.
[6] A. Montoya, F. Mondragon, T.N. Truong. *Fuel Process. Technol.,* **2002;** *77*(Special Issue SI), 453–458.
[7] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A.J. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G.Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople. *Gaussian 98, Revision A.9*, Gaussian, Inc.: Pittsburgh, PA, **1998**.
[8] A. Montoya, T.N. Truong, A.F. Sarofim. *J. Phys. Chem. A,* **2000;** *104*(26), 6108–6110.
[9] T. Kyotani, A. Tomita. *Prepr. Symp. – Am. Chem. Soc., Div. Fuel Chem.,* **2000;** *45*(2), 221–224.
[10] A. Montoya, F. Mondragon, T.N. Truong. *Fuel Process. Technol.,* **2002;** *77*(Special Issue SI), 125–130.
[11] Z.H. Zhu, J. Finnerty, G.Q. Lu, R.T. Yang. *Energy Fuels,* **2002;** *16*(6), 1359–1368.
[12] P. Garcia, A. Molina, F. Mondragon. *Carbon,* **2005;** *143*, 445–1452.
[13] K.J. Huettinger, J.S. Nill. *Carbon,* **1990;** *28*(4), 457–465.