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Fuel Processing Technology 77–78 (2002) 125–130

FUEL
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Formation of CO precursors during char gasification with O₂, CO₂ and H₂O

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Received 4 February 2002; received in revised form 12 February 2002; accepted 14 February 2002

Abstract

The nature of some of the carbon–oxygen complexes formed after chemisorption of O₂, CO₂ and H₂O on carbonaceous surfaces was determined. The analysis was done by means of density functional theories. Among the three reactions studied, CO₂ chemisorption is the less exothermic. The nature of carbon–oxygen complexes depends on the oxidant agents. However, surface transformations of those complexes produce common surface oxygen groups that can desorb CO. Therefore, new data are presented to get insight into a unified mechanism of uncatalyzed carbon gasification. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gasification; Chemisorption; Molecular simulation; Surface oxygen complexes

1. Introduction

The noncatalytic oxidation of carbonaceous materials yields carbon–oxygen complexes which are formed in the presence of oxidizing agents such as H₂O, CO₂, and O₂. Carbon–oxygen complexes have attracted attention in recent years due to the lack of a detailed mechanism for combustion and gasification of carbonaceous materials. Characterization and surface transformation of the carbon–oxygen groups from unstable to stable complexes is important.

There have been several studies attempting to identify the chemical nature of surface complexes on carbonaceous materials providing a broad spectra of oxygen groups as

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reviewed elsewhere [1]. Some of these studies have provided evidences for an unified basis of reaction mechanism for carbon gasification [2–4], particularly from CO temperature programmed desorption profiles [5]. Few studies have attempted to make an analysis at the molecular level on the nature of surface complexes formed by different oxidizing agents. The difference in the intrinsic reactivity of H₂O, CO₂ and O₂ and the relative significance of the oxygen complexes in the gasification reaction has not been well explain so far. Here we present molecular level characterization of some of the carbon–oxygen complexes formed with different oxidizing agents as well as their dynamic transformations on the surface that can provide further evidences for the unified view of the gasification mechanism.

2. Model of calculation

Carbonaceous models and carbon–oxygen complexes were fully optimized at the B3LYP density functional theory level [6] using the 6–31G(d) basis set. Unrestricted open-shell wave function was used in all open-shell cases. Calculations were carried out on the ground state. All calculations were done using the GAUSSIAN 98 program.[7]

3. Results and discussion

Chemisorption of CO₂, H₂O and O₂ can be represented as follows, where C_f symbolize a surface chemisorption site and C(x) symbolize a surface bound oxygen complex



Reactions (R1–R3) were simulated on a seven 6-member ring carbon model in zigzag shape to represent a carbonaceous surface. Some carbon atoms at the edge of the carbon model are left unsaturated to simulate chemisorption sites. Since the reaction of CO₂, H₂O and O₂ with carbonaceous surfaces usually take place at high temperatures, they can be vibrationally excited particularly in the low frequency bending modes suggesting different possible adsorption configurations. However, we have focused just on the adsorption on the edge of the carbon model since it is known to be energetically more favorable adsorption pathways. Four different oxygen groups were obtained by the chemisorption process namely, phenol, peroxide, lactone and a heterocyclic compound. The model and selected optimized geometrical parameters are presented in Fig. 1. Normal mode analyses show that these carbon–oxygen complexes are stable structures with all real frequencies. Adsorption of H₂O, CO₂ and O₂ yields different carbon–oxygen complexes depending on the chemical nature of the oxidant agent. CO₂ can form

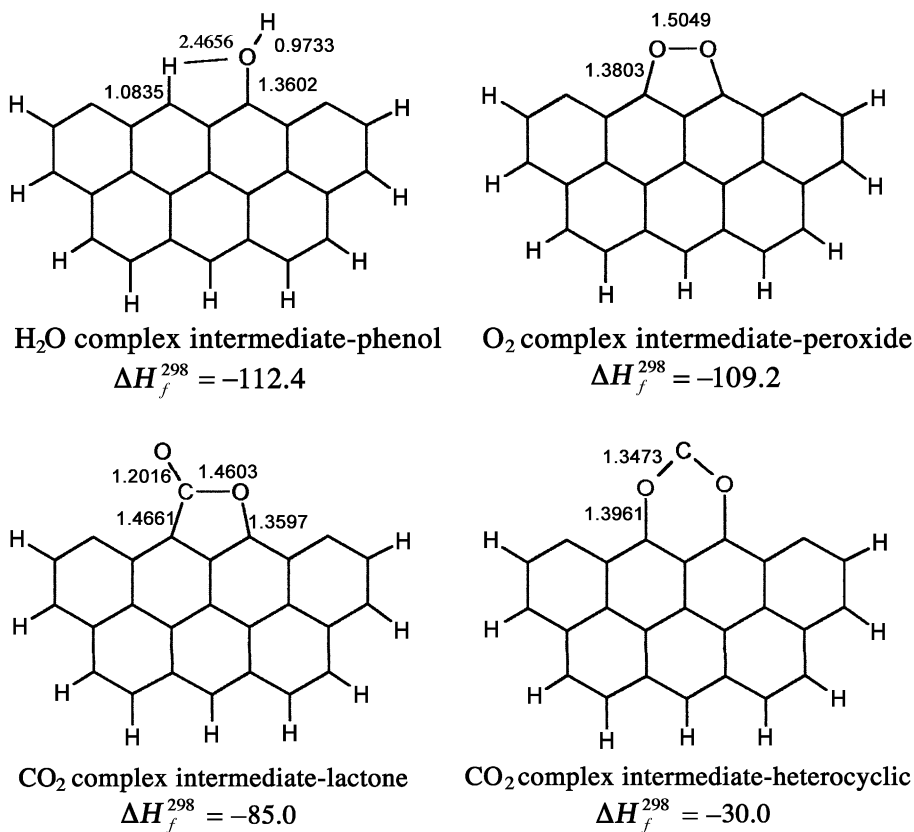
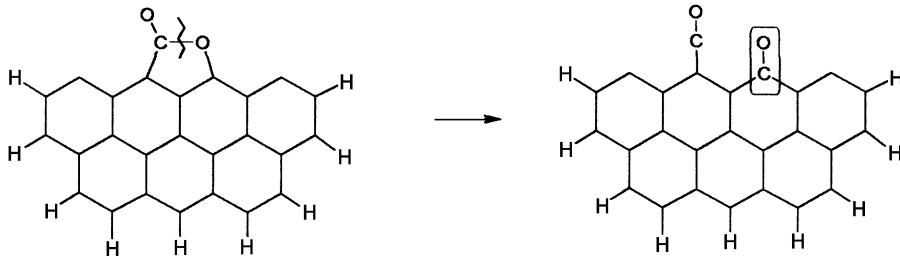


Fig. 1. Surface carbon–oxygen complexes formed after H₂O, O₂ and CO₂ chemisorption on a carbonaceous surface. Optimized bond lengths in Å. Heats of adsorption in kilocalorie per mole.

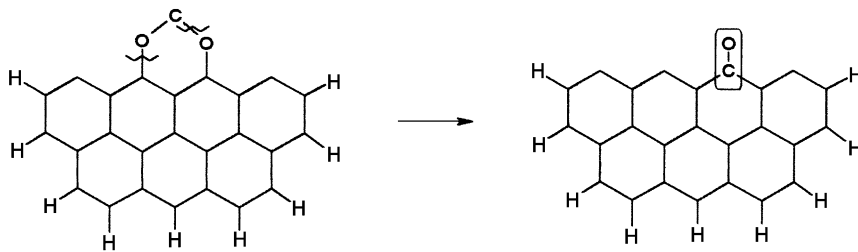
lactones and heterocyclic complexes while H₂O and O₂ can form phenols and peroxide surface complex, respectively. Oxygen and carbon dioxide are adsorbed molecularly while water can dissociatively be chemisorbed to form OH species. The heats of formation at 298 K of the oxygen complexes are also shown in Fig. 1. They were obtained as the difference between the optimized energy corrected by the enthalpy energy at 298 K of the product and reactants. Note that formations of all four carbon–oxygen complexes are exothermic. CO₂ chemisorption reaction is the less exothermic because the lactone and the heterocyclic carbon–oxygen complexes have the lowest heat of adsorption. However, due to the large value of the heat of adsorption of the initial oxygenated complexes, their chemical nature can transform into more stable complexes. For example, the peroxide complex can transform into two stable semiquinone groups by dissociating the O–O bond.

We have examined systematically transformations of the carbon–oxygen complexes described above into stable semiquinone groups. Since these carbon–oxygen complexes

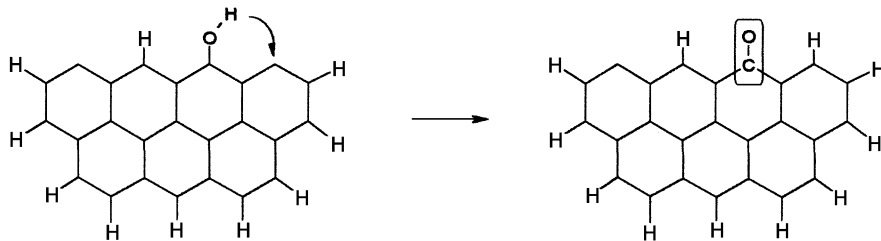
a) $\Delta H_r^{298} = +16.7$



b) $\Delta H_r^{298} = +5.7$



c) $\Delta H_r^{298} = -63.9$



d) $\Delta H_r^{298} = -49.3$

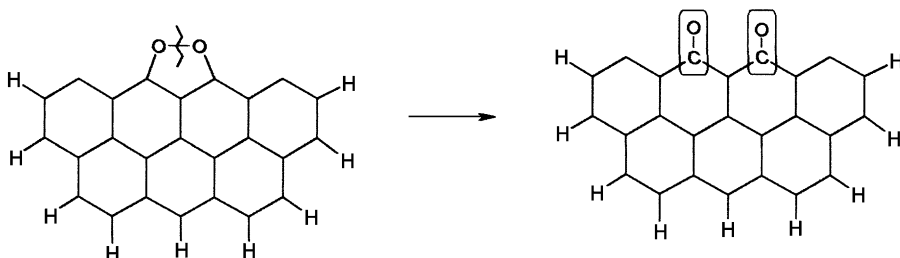


Fig. 2. Surface transformation reactions to semiquinone groups. Heats of reactions are in kilocalorie per mole.

were produced by three different oxidants such transformations would yield valuable information for developing the unified mechanism for gasification. These transformations are presented in Fig. 2, along with their corresponding heats of reaction. Notice that other surface transformations can also occur but they were not analyzed here. All of the structures were fully optimized and a normal mode analyses were carried out to determine the nature of the carbon–oxygen complex. Heats of reaction were obtained by the energy differences between the optimized reactant and products corrected by the enthalpy energies at 298 K. It is seen that CO₂ complexes, namely lactone and the heterocyclic compound, can transform into semiquinone groups by an endothermic process. However, the energy required for such transformation is much smaller than the energy released during the complex formation (heats of adsorption), thus such transformations are thermodynamically possible. Transformations of H₂O and O₂ complexes into semiquinone groups are thermodynamically favorable via exothermic processes. Although complete reaction path analyses were not done, it is possible from the above results to conclude that different surface complexes can generate both carbonyl and semiquinone groups. Since the semiquinone group is much more stable compared to the carbonyl group it becomes a common rate-limiting step during gasification.

We have examined the desorption of CO from carbonyl and semiquinone oxygen complexes using both density functional theory and direct ab initio dynamics method for predicting thermodynamic and kinetic properties from first principles [8,9]. Notice that semiquinone groups in Fig. 2 are surrounded by different chemical environments. We have found that CO desorption energy is affected by the surface environment and surface coverage [8] allowing a broad peak in the CO temperature desorption spectra as it is obtained experimentally [3,5]. It is important to point out that CO desorption from semiquinone oxygen groups is the rate-limiting step but it is not the only source of CO in carbon gasification. Other oxygen groups like carbonyl and ether can also produce CO. A more complete study is in progress.

4. Conclusions

The nature of carbon oxygen complexes was analyzed by means of quantum chemical density functional theory. Chemisorption of different oxidant agents on a clean carbon surface form different carbon–oxygen complexes. From heats of adsorption, surface transformations of such oxygen complexes are possible and can yield similar common surface oxygen species such as semiquinone groups. The results suggest that it is possible to develop an unified mechanism for carbon gasification.

Acknowledgements

T.N. Truong acknowledges the financial support from NSF and the University of Utah. F. Mondragón and A. Montoya thank COLCIENCIAS and the University of Antioquia for financial support of project no. 1115-05-10853. We also thank the Utah Center for high-performance computing for computer time support.

References

- [1] H.P. Boehm, *Carbon* 32 (5) (1994) 759–769.
- [2] J.A. Moulijn, F. Kapteijn, *Carbon* 33 (8) (1995) 1155–1165.
- [3] P.J. Hall, J.M. Calo, H. Teng, E.M. Suuberg, J.A. May, W.D. Lilly, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 34 (1989) 112–120.
- [4] N. Chen, R.T. Yang, *J. Phys. Chem. A* 102 (31) (1998) 6348–6356.
- [5] B. Marchon, J. Carrazza, H. Heinemann, G.A. Somorjai, *Carbon* 26 (4) (1988) 507–514.
- [6] A.D. Becke, *J. Chem. Phys.* 98 (7) (1993) 5648–5652.
- [7] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al, *Gaussian, Inc., Rev. A.9*, Pittsburgh PA, 1998.
- [8] A. Montoya, T.-T.T. Truong, F. Mondragón, T.N. Truong, *J. Phys. Chem. A* 105 (27) (2001) 6757–6764.
- [9] A. Montoya, F. Mondragón, T.N. Truong, *J. Phys. Chem. A* 106 (16) (2002) 4236–4239.