

CO DESORPTION FROM CARBONYL SURFACES SPECIES IN THE GASIFICATION OF COAL

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Introduction

The reactivity behavior of chars and carbons under reaction with oxygen agents has been the focus of many studies due to its practical applications in industry. Characterization of the oxygen complexes in the char surface is very important because its relation with mechanism of gasification and combustion reactions. Studies using transient kinetic have shown that in the char-CO₂ and char-O₂ reactions, there must be at least two kinds of surface oxygen complexes that release a CO molecule to the gas phase.¹⁻⁴ Temperature Programmed Desorption (TPD) experiments from oxidized carbons and chars have observed different surface oxygen complexes depending on the temperature at which they are desorbed. It has been suggested that the broad TPD feature in the CO desorption can be due to the surface heterogeneity of the char. Semiquinone and ether groups have been proposed to account for the CO molecule desorption at high temperature^{5,6} while carbonyl groups for the CO molecule desorption at low temperature.⁷

Our goal is to employ a state-of-the-art quantum chemistry method to address several fundamental questions regarding the desorption of carbonyl-type surface species. In particular, we examined the effects of the surface inhomogeneity from the presence of different active site structures such as arm-chair, zigzag and tip shapes and how it correlates to the observed TPD peak.

Computational Details

Physical models. Different carbonyl models with different sizes and shapes that can be found in typical carbonaceous structure were proposed and are presented in Figure 1. Model **A** represents a carbonyl group in a tip shape, model **B** represents a carbonyl in an arm-chair shape and model **C** represents a carbonyl in a zigzag shape. Models considered in this study represent different local environments of the carbonyl group and the effect of the surface heterogeneity of the char in the desorption energy. Some carbon atoms are numbered to facilitate the discussion below.

Theoretical model. We have used the hybrid B3LYP DFT functional level of theory^{8,9} using the 6-31G(d) basis set to calculate CO desorption energies and geometry of the carbonyl models and products of CO molecule desorption. Unrestricted Open-Shell wave function was used in all open-shell cases because the spin contamination in the unrestricted B3LYP is reasonably small and has acceptable small effects on the energetic properties of graphene layers.¹⁰ Single-point energy calculations were performed at the same level of theory for different electronic states for each molecular model, the ground state was selectively chosen to be the lowest energy one. All calculations were done using GAUSSIAN 98.¹¹

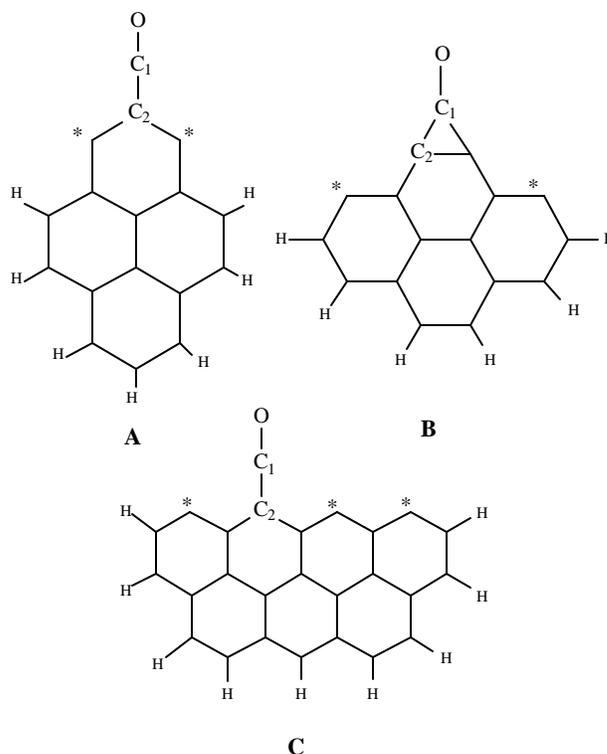


Figure 1. Geometry of the carbonyl models selected. (*) Active sites.

Results and discussion

All geometrical parameters in all equilibrium structures, namely surface oxygen complexes, char models and CO molecule were fully optimized except for the carbonyl bond angle C₂-C₁-O of surface oxygen complexes with the zigzag and tip shape models. This angle was frozen at 180 degrees in order to simulate the carbonyl surface complexes. It is possible that in such models the oxygen of the carbonyl group can migrate to a neighboring active site to form a cyclic ether group. Such a migration will be investigated in a separate study.

We found that the carbonyl surface complexes have planar structure as shown in Figure 1. Selected optimized geometrical parameters and bond orders obtained with the theory of atoms in molecules¹² are listed in the Table 1.

Table 1. Optimized Bond Lengths (BL in pm) and Bond Orders (BO) of the Carbonyl Surfaces Species

Parameters		Carbonyl model		
		Tip-shape	Arm-chair	Zig-zag
C ₁ -O	BL	114.8	120.4	116.6
	BO	1.59	1.43	1.56
C ₁ -C ₂	BL	137.0	144.2	133.6
	BO	1.28	1.20	1.57

As can be seen, The C₁-O and C₁-C₂ bonds of the arm-chair model are the longest bonds in the models studied. It is because the carbonyl group in the arm-chair model forms a three member ring with the six-member ring and increases the bond lengths to stabilize the ring. The C₁-C₂ bond order for the tip and arm-chair models are much smaller than the C₁-C₂ bond order in the zigzag model. It shows a possible CO molecule desorption from the tip and arm-chair models by breaking the C₁-C₂ bond. Carbonyl in the zigzag model has a very strong C₁-C₂ bond order, suggesting two channels of reaction. One, desorption of CO with a high energy barrier. Second, an oxygen migration from the carbonyl group to the carbon model forming an ether group with a nearby active site.

The desorption energy can be calculated by the difference between the total energy of the optimized product and that of the reagent. Table 2 lists the desorption energy of the CO molecule from the carbonyl models.

Table 2. Desorption Energy (kcal/mol) of the CO Molecule from Carbonyl Models

Carbonyl Model	Desorption energy
Tip-shape	13.1
Arm-chair	38.1
zig-zag	53.3

The CO molecule desorption process is an endothermic reaction where the energy barrier depends on the shape of the active site of the carbonyl group rather than in the size of the carbon model. For instance, models in tip and arm-chair with the same number of six-member rings have different CO desorption energies. The CO desorption energy is related to the C₁-C₂ bond order. The larger the C₁-C₂ bond order, the higher the CO molecule desorption energy becomes. Three different CO molecule desorption energies can be identified. Models in tip shape have the lowest CO desorption energy barrier and models in zigzag shape have the highest CO desorption energy barrier. The energy barrier for the CO molecule release increases in the order, tip shape < arm-chair shape < zigzag shape. These three different energy barriers can explain the experimental broad TPD feature of the CO molecule desorption from oxidized carbons.

The CO desorption energy from carbonyl groups was also studied in the presence of different oxygen complexes C(O). Model in zigzag shape was selected due to the highest energy barrier. A semiquinone group was placed near to the carbonyl model and the CO desorption energy was obtained. Figure 2 shows the geometry of the reactants and products.

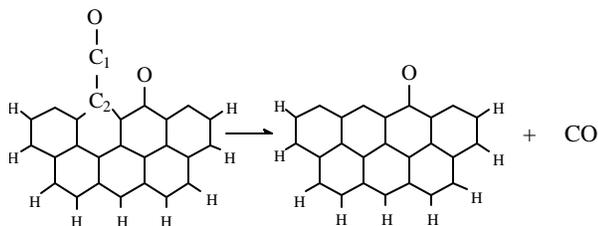


Figure 2. Geometry representation of the CO molecule desorption from carbonyl groups near to different oxygen species.

Similarly the geometries of the reagent and carbon product were fully optimized except the C₂-C₁-O carbonyl angle and the C-C-O semiquinone angle. They were frozen at 180 and 120 degrees, respectively, in order to avoid the formation of the lactone group which will be addressed in a separate study. The product of reaction leaves a semiquinone group in the carbon model, which can be released as CO molecule with a different desorption energy. In this case, the CO desorption energy is 43.0 kcal/mol showing that the semiquinone group decreases the CO desorption activation energy by 10 kcal/mol. This indicates that the CO molecule desorption depends not only on the local active site but also on the presence of different oxygen complexes near to the carbonyl group.

Conclusion

The desorption of a CO molecule from carbonyl surface species depends specially on the local active site of the carbonyl group. Our study of different local structures of the active site shows that the CO desorption energy can spread from 13 to 54 kcal/mol and can explain the broad feature in the TPD spectra. Furthermore, the presence of a nearby oxygen complexes can strongly affect the desorption kinetics of the carbonyl group.

Acknowledgements. F.M. and A.M want to thank Colciencias and the University of Antioquia for financial support of the project No 1115-05-10853. TNT acknowledges financial support from NSF. We also thank the Utah Center for High Performance computing for computer time support.

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