CO_2 ADSORPTION ON CARBONACEOUS SURFACES: A COMBINED MOLECULAR MODELING AND EXPERIMENTAL STUDY

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Introduction

Gasification of coke, char and graphite with CO_2 has been a research focus for several decades. However, our understanding on the mechanism of this industrial important process is still limited. For instance, the mode of adsorption of CO_2 on carbanaceous surfaces, i.e. a molecular or dissociative adsorption, is not known for certain, Though, it is generally believed that CO_2 is chemisorbed on the carbon surface to release a CO molecule to the gas phase leaving a chemisorbed oxygen atom on the carbon surface forming a Carbon-Oxygen complex.[1,2] There have been a number of experimental studies attempting to identify surface oxygen complexes due to its importance in deducing the mechanism of these reactions.[3-5] Surface oxygen complexes such as pyrone, semi-quinone, carbonyl, ether, lactone, and acid anhydride have been proposed so far. However, there has been no definitely conclusion regarding the relative significance of these oxygen complexes in the gasification reactions and the chemical transformations between them.

In the present study, we have carried out a combined theoretical and experimental study on the adsorption of CO_2 on char. In particularly, theoretical study using a state-of-the-art quantum chemistry method, namely non-local hybrid density functional theory, was performed to determine stable CO_2 adsorption complexes and to characterize them. Such computational tool has been previously applied to gasification and combustion reactions.[6-8] Heat of adsorption of CO_2 on char was determined experimentally using the volumetric technique and it is compared to the theoretical prediction. Such comparison allows us to elucidate molecular structures and stability of the surface complexes.

Experimental

CO_2 isosteric heat of adsorption on cellulose char. In order to compare the theoretical data of CO_2 adsorption energy on carbon models, we have determined the isosteric heat of CO_2 adsorption on cellulose char at moderated temperatures. Cellulose was chosen in this experiment to provide clean char and to avoid problems associating with mineral matter contaminations. Preliminary experiments were carried out in a thermogravimetric equipment at 1 atm using high purity CO_2 to determine the temperature at which the CO_2 is chemisorbed without gasifying the char. The change in the char weight was used as a guide to determine the CO_2 chemisorption. A fresh sample of cellulose char was then subjected to CO_2 adsorption at constant temperature in a volumetric equipment in the range of 10 to 650 torr. The isosteric heat of adsorption was determined at different CO_2 coverage on cellulose char using the Clausius-Clapeyron equation.

Computational Details

Structures and adsorption energies of several surface oxygen complexes were determined using the B3LYP DFT level of theory[9,10] with the 6-31G(d) basis set. 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.[11] Single-point energy calculations were performed at the same level of theory for different electronic states on each molecular model, the ground state was selectively chosen to be the one with lowest energy. Char is modeled by a seven-ring single-layer graphene molecule with unsaturated carbon atoms to represent the active sites. All calculations were done using GAUSSIAN 98.[12]

Results and Discussion

Isosteric heat of adsorption. It was found that cellulose char gains ≅ 0.5% of its weight in the range of 653-693 K in CO_2 atmosphere. Above 773 K, the char begins to lose weight slowly. Thus, CO_2 adsorption at different pressures was carried out at 653, 673 and 693 K in a volumetric equipment. The volume adsorbed at different pressures was converted to heat of adsorption using the Clausius-Clapeyron equation. The isosteric heat of CO_2 adsorption at different loading on cellulose char is shown in the Figure 1.

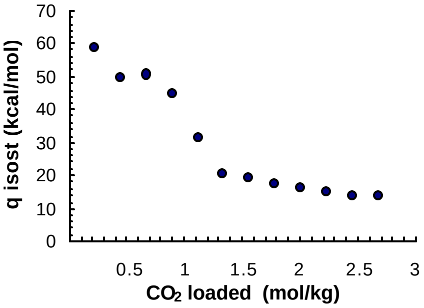


Figure 1. Isosteric heat of CO_2 adsorption on cellulose char at different CO_2 loading in the range of 653-693 K**.**

The CO_2 adsorption was found to be an exothermic reaction at the temperature used. The isosteric heat as a function of CO_2 loading can be separated into two regions. The low loading region from 0.22 to 1.3 mol/kg, the isosteric heat of adsorption decreases rapidly from 60 to about 20 kcal/mol whereas the high-loading region above 1.3 mol/kg the heat of adsorption from 13-20 kcal/mol becomes nearly independent of loading. This indicates that in the low-loading region, CO_2 molecules chemisorb at the available active sites to form stable surface oxygen species when all of the active sites are covered, CO_2 molecules physisorb to char either on the graphene planes or to the surface oxygen complexes. Note that the lowest CO_2 loading data in Figure 1 is 0.22 mol/kg. It corresponds to ≅ 10 torr of CO_2 pressure. The isosteric heat of adsorption is expected to increase at lower surface coverage.

Theoretical results. A zigzag carbon model was used initially to study CO_2 adsorption as represented in the Figure 2. Other carbon models such as the arm-chair or tip-shape models are currently under investigation. The zigzag model was fully optimized in its ground state and several CO_2 adsorption modes were studied on the region marked with dashed lines. Particularly, four different CO_2 modes of adsorption shown in Figure 3 were investigated. These four modes of adsorption resulted in three oxygen complexes.

A lactone group was formed by the CO_2 orientations number 1 and 3. An ether group was formed by the CO_2 orientation number 2 and a carbonyl-type group was formed by the CO_2 orientation number 4.

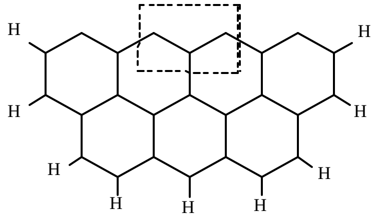


Figure 2. Zigzag carbon model selected for the CO_2 adsorption.

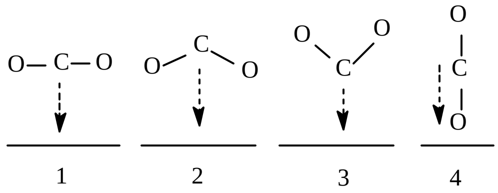
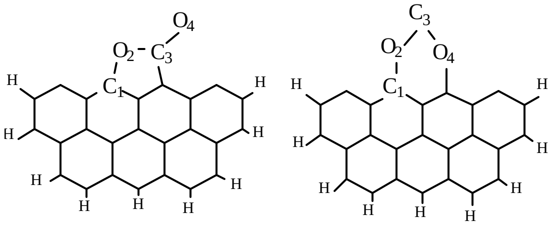


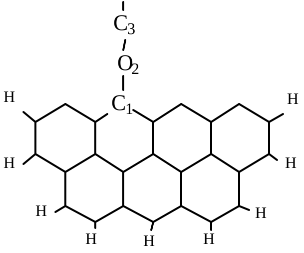
Figure 3. Different CO_2 modes of adsorption to the carbon model.

The geometry of the intermediates is shown in the Figure 4. All of the oxygen complexes were found to be planar. Lactone group forms a five-member ring with the carbon model while the ether group forms a six-member ring with the carbon model.



lactone oxygen complex

Ether oxygen complex



Carbonyl-type oxygen complex

Figure 4. Geometrical representations of the oxygen complexes obtained after the CO_2 adsorption on zigzag carbon model.

The selected important optimized geometrical parameters are shown in Table 1. It shows the bond lengths of the oxygen group region. In all cases, the C_1-O_2 bond binds the CO_2 molecule to the carbon model. As can be seen, lactone and ether groups have the shortest C_1-O_2 bond lengths while the carbonyl-type model has a very long C_1-O_2 bond. On the contrary, O_2-C_3 and C_3-O_4 bond lengths are the lowest in the carbonyl-type model, suggesting that the CO_2 approach number 4 to the zigzag model, does not perturb the CO_2 molecule character after it has been bound.

The CO_2 adsorption energy predicted for the formation of the lactone, ether and carbonyl-type oxygen complexes where –91.5, –34.5 and +72.7 kcal/mol, respectively.

Table 1. Geometrical Parameters After the Optimization Procedures

Oxygen complex	Bond length (pm)		
	C_1-O_2	O_2-C_3	C_3-O_4
Lactone	136.0	146.0	120.2
Ether	139.6	134.7	134.7
Carbonyl-type	142.2	119.7	117.8

From the energetic argument we can reject the carbonyl-type oxygen complex to be a possible stable species. The formation of lactone and ether groups is an exothermic process and is consistent with our experiment. In order to compare with the experimental heat of adsorption we must include at least the zero-point energy corrections to the calculated adsorption energies. Such corrections currently under investigation would decrease the adsorption energies and bring the calculated results in better agreement with our experimental data.

Conclusions

It was found a molecular CO_2 adsorption on zigzag carbon models to form ether and lactone groups as stable oxygen complexes. Lactone is energetically more favorable than ether group and is an important group in the gasification at low temperatures. More detailed investigation on other surface oxygen complexes using different carbon models to model surface heterogeneity is currently being performed and will be reported in a forthcoming paper.

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