



Universidad de Concepción
Dirección de Postgrado
Facultad de Ingeniería - Programa de Doctorado en Ciencias de la Ingeniería con
Mención en Ingeniería Química

**Termoquímica y cinética de las reacciones de transferencia
de oxígeno sobre la superficie de grafeno:
comparación de interacciones entre NO, O₂, H₂O y CO₂ y
sitios activos de tipo carbeno**

**Thermochemistry and kinetics of oxygen transfer reactions
on the graphene surface:
A comparison of interactions between NO, O₂, H₂O and CO₂
and carbene-like active sites**

Tesis para optar al grado de Doctor en Ciencias de la Ingeniería
con mención en Ingeniería Química

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Summary

Because of the wide-ranging applicability of solid carbon in the energy and materials industry as well as their similarities, we have analyzed its oxygen-transfer reactions in great detail using quantum chemistry procedures. We compared their mechanistic similarities and differences by obtaining thermochemical and kinetic information using the density functional theory (DFT) as implemented in the Gaussian 03 software package. The functional and basis set used, B3LYP and 6-31g(d), were confirmed to be a good compromise between accuracy and computational time. The model used to represent the carbon surface consists of small graphene clusters with zigzag active sites at the graphene edge. Mechanistic paths are proposed after analyzing the similarities and differences among the four reactions, as well as their comparison with experimentally determined facts. Frontier orbital theory was used to assess reactivity differences. A complementary study regarding the nature of active sites and the electron density distribution at a zigzag graphene edge was also performed, by including periodic boundary conditions (PBC) to model graphene nanoribbons (GNRs).

The reactions paths are dependent on the number of sites available. A C(O) surface intermediate is common to all reactions, whereas the formation of a C(O₂) intermediate is important only for the reactions with O₂ and NO dimer. Molecular oxygen can react with one or two sites to produce C(O₂) or C(O), respectively. The NO monomer can react with two or three contiguous sites to produce C(O); interaction with one site inhibits the reaction. The NO dimer reacts at low temperatures to form C(O₂) or C(O) complexes by a sequential electron pairing process and also by N₂O intermediate formation; water vapor can react with one or two sites to form C(O) complexes in an exothermic reaction, but the H₂ desorption from the hydroxyl intermediate requires a more saturated surface which also becomes the process more endothermic; carbon dioxide can react with one site to form the C(O) intermediate or with two sites to form a C(CO)C(O) bonded complex (CO₂+2C=C(CO)C(O)), which are highly stable and need high temperatures to desorb the CO final product.