Interconversion and Extrusion of the Sulfur Dioxide Reduction Intermediates Inserted on Graphene Oxide

Eduardo Humeres,[a] Alessandra Smaniotto,[a] Luís Otávio B Benetoli,[a]
Karen M. de Castro,[a] Nito A. Debacher,[a] Wido Schreiner.[b]

[a] Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, Brazil.
eduardo.humeres@ufsc.br
[b] Departamento de Física, Universidade Federal do Paraná, Curitiba, PR, Brazil.

The SO_2 reduction on carbons occurs through stable reactive intermediates chemically bound to the carbon matrix, as oxidized sulfur (1,3,2-dioxathiolane in equilibrium with 1,2-oxathietane 2-oxide) and non-oxidized sulfur (episulfide). The SO_2 reduction proceeds through a primary mechanism where upon the adsorption of SO_2 on a zigzag diradical hedge the carbon matrix, the oxidized intermediates decompose to produce an episulfide and a peroxide that decomposes to CO_2 in a further step. Graphene oxide sheets, obtained by oxidation of graphite microparticles by strong acids followed by thermal exfoliation, were treated with non-thermal plasma under a SO_2 atmosphere, at room temperature. The XPS spectrum showed that SO_2 was inserted only as oxidized intermediate at 168.7 eV in the S2p region. Short thermal shocks at 600 and 400 ^oC, under Ar atmosphere, produced reduced sulfur and carbon dioxide. Refluxing this material in CS_2 (b.p. 46 ^oC) resulted in sulfur elimination and interconversion of the intermediate into oxidized intermediate with no decarboxylation, as shown by the XPS spectrum and TGA analysis coupled to FTIR. Mechanisms for these reactions were postulated using the atom inventory method. These results support the hypothesis, based on theoretical calculations, that there are two major groups of reactions with different energetic demand in the sulfur dioxide reduction on carbons. The energy barrier for the interconversion between the sulfur dioxide reduction intermediates and sulfur extrusion from the matrix is much lower than the energy barrier for decarboxylation.

Acknowledgements. CAPES, CNPq