

# CARBON OXIDATION MECHANISMS: EXAMPLES OF MACROSCOPIC COMPLEMENTARITY PRINCIPLE?

L. R. Radovic, M. Karra and K. Skokova

Department of Materials Science and Engineering  
Fuel Science Program  
The Pennsylvania State University, University Park, PA 16802

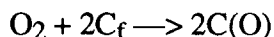
## INTRODUCTION

Despite its admirable usefulness, the venerable Arrhenius expression has many limitations when used to describe the kinetics of heterogeneous gas-solid reactions in general, and of carbon oxidation in particular. This becomes especially evident when one attempts to rationalize the reactivity differences of different carbons in the same reactive environment, or those of the same carbon doped with different catalysts or inhibitors.

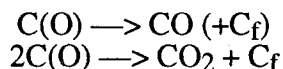
The present communication is a first step in our attempt to formulate the criteria for a judicious modification of the Arrhenius rate expression. It resorts to the same argument embodied in Bohr's microscopic complementarity principle (1), i.e., that the use of mutually exclusive concepts is sometimes (or always?) necessary for a complete understanding of a phenomenon.

## CARBON OXIDATION

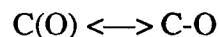
The applicability of the complementarity principle to the mechanism of carbon oxidation is obvious, at least in a qualitative sense. It is well known that carbon oxidation (and gasification in general) proceeds through the formation of carbon-oxygen surface complexes on free carbon reactive sites ( $C_f$ ):



The fate of these surface complexes is now well understood, both qualitatively and quantitatively, for both graphitic and turbostratic carbon materials (2-5). Some surface complexes decompose immediately to form CO and CO<sub>2</sub>:



Others have a much longer residence time on the surface (e.g., on the basal plane). Their kinetic and mechanistic importance can be expressed in several ways, of which the simplest one seems to be the following (3):



In other words, some reactive intermediates (or 'labile' complexes) are converted to 'stable' C-O complexes that inhibit (temporarily) the oxidation reaction. The reverse process becomes dominant in the latter stages of the reaction as the carbon is completely consumed. Thus carbon-oxygen surface complexes are both catalysts and inhibitors of carbon oxidation (3,6). The formulation of an appropriate quantitative expression for this complex kinetic relationship is a subject of ongoing research.

## EFFECT OF BORON ON OXIDATION

Inhibition of carbon oxidation by boron or boron-containing compounds is well known (5,7-9). While the site-blocking and diffusion-retarding effects of a B<sub>2</sub>O<sub>3</sub> film (formed on the carbon surface during oxidation) seem to be straightforward, the role of substitutional boron is quite unclear. The majority of experimental evidence indicates that it inhibits carbon oxidation. This inhibition has been attributed, rather vaguely, to an electronic effect: boron incorporation into the graphite lattice results in a redistribution of  $\pi$  electrons that retards CO (and CO<sub>2</sub>) desorption (8,9).

Close examination of the experimental data available in the literature, as well as our own recent results (10), show that boron acts as both inhibitor and catalyst of carbon oxidation. While this provides another example of the macroscopic complementarity principle, its explanation is the subject of ongoing experimental and theoretical research. A tentative analysis is offered below.

The results of straightforward Hückel molecular orbital theory calculations (10) for a crystallite containing 150 carbon atoms show that, at 0.67% substitutional B, the C-C bonds are weakened and the C-O bond is strengthened. Boron is thus predicted to catalyze CO (and CO<sub>2</sub>) desorption. On the other hand, because

substitutional boron does not contribute an electron to the delocalized  $\pi$  system of the graphene layer, it is known to decrease the Fermi level of graphite (7). It is conceivable that oxygen's affinity toward carbon also decreases to some extent, thus inhibiting O<sub>2</sub> adsorption. This is analogous to the opposite effect of potassium, which lowers the work function of carbon and increases the dissociation probability of O<sub>2</sub> (11).

## COMPENSATION EFFECT

When all the experimental and/or mathematical artifacts are accounted for, there remain quite a few possible physicochemical explanations for this seemingly ubiquitous effect in chemical kinetics (12-18). These explanations are not necessarily mutually exclusive. In fact, they may all be pointing in the same direction: the same factors that cause a decrease in the observed activation energy (e.g., of adsorption) are responsible for a concomitant decrease in the preexponential factor (e.g., number of carbon reactive sites). Once again, we witness the mutually exclusive, yet complementary effects of catalysis and inhibition. This experimental fact is an important discriminatory tool in formulating the 'right' kinetic expression for carbon oxidation. For example, as the surface coverage increases, the rate-determining step may shift from adsorption toward desorption; the latter is known to have a higher activation energy than the former.

## MACROSCOPIC COMPLEMENTARITY

Bohr himself has indicated that the complementarity principle should be relevant in fields outside physics (1). He identified explicitly one such field: the psychological relationship between 'spectators' and 'actors' in the "great drama of [human] existence. [...] These two modes of engagement are both necessary elements in the person's mental content, yet they exclude each other - they are complementary" (1). Obviously, at the present level of human knowledge, this macroscopic complementarity principle escapes easy quantification and remains in the realm of philosophy. Others, however, may be much more amenable to quantitative analysis, but such an approach does not seem to have been pursued. One notable exception is the work of Prigogine, in which the complementarity between thermodynamics and dynamics (or, more poetically stated, between being and becoming) is

studied using nonequilibrium thermodynamics and formulated using a quantum theory of irreversible processes (19,20).

We submit that (a) the role of carbon-oxygen surface complexes, (b) the effect of boron on carbon reactivity and (c) the compensation effect - important phenomena in carbon oxidation that have eluded definitive explanation - need to be formulated in accordance with the macroscopic complementarity principle.

## REFERENCES

1. A. Pais, "Niels Bohr's Times," Clarendon Press, Oxford, UK, 1991.
2. N.R. Laine, F.J. Vastola and P.L. Walker, Jr., *J. Phys. Chem.* **67**, 2030 (1963).
3. A.A. Lizzio, H. Jiang and L.R. Radovic, *Carbon* **28**, 7 (1990).
4. P.L. Walker, Jr., R.L. Taylor and J.M. Ranish, *Carbon* **29**, 411 (1991).
5. J. Lahaye and P. Ehrburger, Eds., "Fundamental Issues in Control of Carbon Gasification Reactivity," Kluwer, Dordrecht, The Netherlands, 1991.
6. M.H. Back, *Carbon* **29**, 1290 (1991).
7. D.J. Allardice and P.L. Walker, Jr., *Carbon* **8**, 375 (1970).
8. L.E. Jones and P.A. Thrower, *J. Chim. Phys.* **84**, 1431 (1987).
9. W. Kowbel, Y. Huang and H. Tsou, *Carbon* **31**, 355 (1993).
10. M. Karra, P.A. Thrower and L.R. Radovic, work in progress.
11. C. Janiak et al., *Langmuir* **9**, 3427 (1993).
12. E. Cremer, *Adv. Catal.* **7**, 75 (1955).
13. F.S. Feates, P.S. Harris and B.G. Reuben, *J. Chem. Soc. Farad. Trans. I* **70**, 2011 (1974).
14. A.K. Galwey, *Adv. Catal.* **26**, 247 (1977).
15. W.C. Conner, *J. Catal.* **84**, 273 (1983).
16. W.C. Conner and J.A. Schwarz, *Chem. Eng. Commun.* **55**, 129 (1987).
17. W. Linert and R.F. Jameson, *Chem. Soc. Rev.* **18**, 477 (1989).
18. W.R. Patterson and J.J. Rooney, *J. Catal.* **146**, 310 (1994).
19. I. Prigogine, "From Being to Becoming", W.H. Freeman, New York, 1980.
20. I. Prigogine, *Int. J. Quantum Chem.* **53**, 105 (1995).