

# Factors Controlling the Mode by Which a Catalyst Operates in the Graphite-Oxygen Reaction

by

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## Introduction

Although it has been well known for many years that a small amount of a metal/metal oxide can alter the rate of the graphite-oxygen reaction dramatically, the factors which control the mode by which the catalyst operates have, for the most part, remained unknown. Using controlled atmosphere electron microscopy, we have established that for a particle to become active, it must be located at an edge or step site and in a wetting condition.<sup>1</sup> However, whether the subsequent attack occurs by channeling or edge recession, has been an unpredictable event. In this paper a rationale is presented to account for the behavioral pattern of a given catalyst and also an argument for the relative lack of activity of the ferromagnetic metals on the graphite-oxygen reaction.

## Results

Figure 1 shows a compilation of data relating to catalyst behavior observed during CAEM studies of various metal/graphite-oxygen systems, as a function of the position of the metal in the Periodic Table. Metals labelled by the shaded areas tend to undergo a spreading action along the graphite edge sites and catalyze the removal of carbon by the edge recession mode. In contrast, metals in the open boxes exhibit a somewhat weaker interaction with graphite, remaining as discrete particles and catalyzing the gasification by the channeling mode. From Figure 1 it can be seen that three of the metals which have been investigated, Ru, Rh and Ir exhibit both forms of attack; edge recession at temperatures below 1000°C and channeling at higher temperatures. These two activity regions have been found to correspond to the existence of oxides as the stable solid phases

IVA	VA	VIA	VIIA	VIII			IB	IIB
Ti	V	Cr		Fe	Co	Ni	Cu	Zn
		Mo		Ru	Rh	Pd	Ag	
		W	Re		Ir	Pt	Au	

Figure 1. Classification of the modes of catalyzed oxidation of graphite by various metals.

at the lower temperatures and the respective metals at > 1000°C.<sup>2</sup>

The final classification of metals are those labelled by the cross-hatching, which do not wet graphite to any significant degree under these conditions and do not exhibit sustained catalytic activity.

## Discussion

Let us first address the issue of why some catalysts chose to attack the graphite by the edge recession mode while others operate by the channeling mode. Reference to the free-energy data for oxide formation, presented in Figure 2, provides the key to this enigma. Metals labelled by

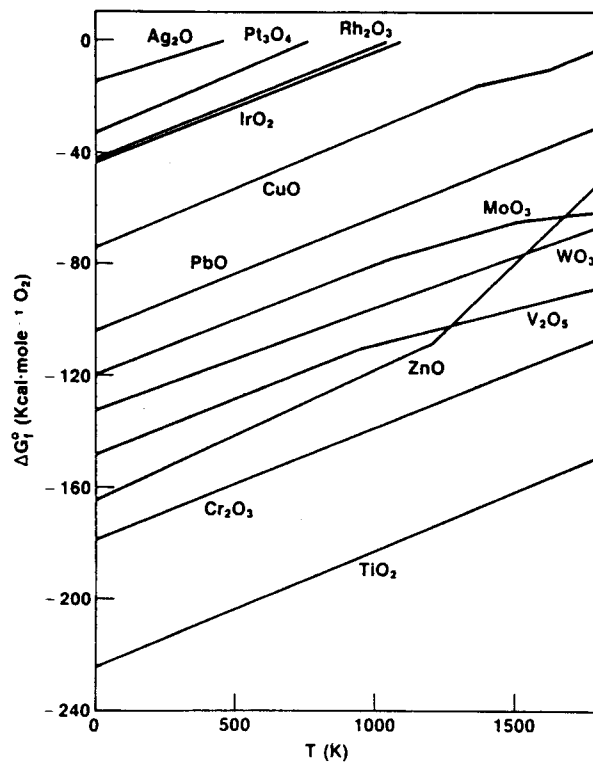
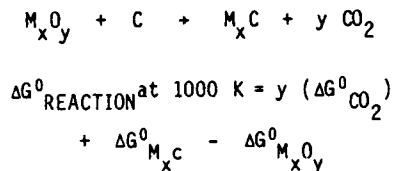


Figure 2. Free energy of formation of oxides.

the shaded areas adsorb oxygen dissociatively and readily form stable oxides. Strong interfacial bonding is expected to occur between this group of metals and the oxygenated carbon edge atoms. The strength of this interaction will be sufficient to induce spreading of the catalyst material along graphite edges and subsequent attack by edge recession. In contrast, metals in the open boxes adsorb oxygen non-dissociatively and tend to remain in the noble state. These metals would not be expected to exhibit a strong interaction with the oxygenated carbon surface allowing the catalyst to exist in the energetically preferred particulate form and attack the graphite via channel propagation. Consistent with these arguments is the finding that catalysts which undergo a transition from oxide to metallic state at high temperature also exhibit a corresponding change in catalytic action from edge recession to channeling.

The relative inactivity of iron, cobalt and nickel for the graphite-oxygen reaction is at first sight perplexing since all three metals form stable oxides, but contrary to the reasonings presented above, do not form a strong interaction with the carbon-oxygen surface. However, when one examines alternate reaction pathways for these metals, a possible explanation for the observed inactivity emerges.

Consider the possibility of converting the "active" metal oxide to an "inactive" metal carbide during interaction with graphite at 1000 K according to the following reaction:



The equilibrium constant, K, can be evaluated as follows:

$$\Delta G^0_{1000} = -RT \ln K$$

This equilibrium constant is directly related to the equilibrium pressure of carbon dioxide:

$$K = (P_{CO_2})^y$$

Hence, one can readily calculate the conditions where the reaction is likely to occur. Values of the equilibrium partial pressures of carbon dioxide have been calculated for systems where the relevant thermodynamic data is available<sup>3</sup> and are listed in Table 1. It is apparent that carbide formation is probable with not only iron and nickel, but also with vanadium and tungsten. Examination of the experimental data from these latter systems does indeed indicate that both elements tend to lose their catalytic activity for the graphite-oxygen reaction at high temperatures.<sup>4,5</sup> Consistent with these arguments is the finding that when the ferromagnetic metals are saturated with carbon, they cease to wet graphite.<sup>6,7</sup>

Table 1. Values of the Equilibrium Partial Pressure of Carbon Dioxide where Relevant Thermodynamic Data is Available.

Oxide	$P_{CO_2, mm}$	Likelihood of Carbide Formation Under CAEM Conditions
TiO <sub>2</sub>	$5.66 \times 10^{-8}$	No
Cr <sub>2</sub> O <sub>3</sub>	$6.69 \times 10^{-6}$	No
MoO <sub>2</sub>	$2.51 \times 10^{-2}$	No
V <sub>6</sub> O <sub>13</sub>	5.98	Yes
WO <sub>3</sub>	$1.58 \times 10^4$	Yes
Fe <sub>2</sub> O <sub>3</sub>	$7.67 \times 10^3$	Yes
NiO	$1.74 \times 10^9$	Yes

If the CO<sub>2</sub> pressure over the sample is less than these equilibrium values, then the carbide formation can occur.

#### Conclusion

One can tentatively conclude that the most efficient catalysts for the carbon-oxygen reaction will be those elements that form stable oxides, but do not readily react with carbon to form carbides. Recent studies by Yang and Wong<sup>8</sup> demonstrate metal carbides do exhibit marginal activity for the graphite-oxygen reaction, but do not function by the conventional modes of attack.

#### References

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