

# The Use of Nonequilibrium Phase Diagrams to Investigate Carbon Formation from Multicomponent Gas Mixtures Over Transition Metals

Albert Sacco, Jr.  
Worcester Polytechnic Institute  
Worcester, Massachusetts 01609

## Introduction

At high temperatures (>450K) if carbon bearing gases come in contact with transition metals or their alloys, carbon deposition often results. Over the past several decades carbon deposition has been a major problem for both transition metal based catalysis and materials of construction. For several years work has progressed in our laboratory on using the control of oxygen, hydrogen, and carbon gas phase activities to control solid (surface?) composition. The work reviewed here is for the transition metal iron exposed to  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$  and  $H_2O$ . The data presented are at high temperatures (>800K) to eliminate the possibility of surface enrichment.

## Methodology

When carbon deposition occurs in multicomponent gas mixtures it is very difficult to determine which solid phase catalyzes carbon deposition. This is due to the fact that during reaction the solid may be oxidized, reduced, or carbided and this may change with time on stream (and even position in the reactor). In such complex systems, gas phase reactions may be catalyzed by solid phases formed during reaction. To handle these kinds of systems it is necessary to control the gas phase chemical potentials (gas phase compositions) during reaction and by so doing favor only the solid phase(s) desired. In this way, it is possible to determine which solid phase(s) catalyze carbon deposition. A convenient way to represent these data and control strategy is illustrated in Figure 1. In Figure 1, the oxidizing, reducing, or carbiding activities are indicated in the regions where the solid iron phase is shown as  $Fe_xO$  (wustite) for oxidizing,  $Fe_3C$  (cementite) for carbiding, and  $\alpha$ -iron for reducing. In addition, the regions in which carbon is thermodynamically predicted to form are also indicated. The curves shown in the Figure represent the  $\alpha$ -Fe/ $Fe_3C$ -gas,  $\alpha$ -Fe/ $Fe_xO$ -gas and  $C_2$ -gas equilibria. Thus if one precarbides the iron sample and feeds a gas mixture represented by point M, one can observe if  $Fe_3C$  catalyzes carbon deposition. In a similar manner an experiment at point X can determine if  $Fe_xO$  catalyzes carbon oxidation.

The data presented here were taken in a differentially operated thermogravimetric reactor with inlet and outlet gas phase composition

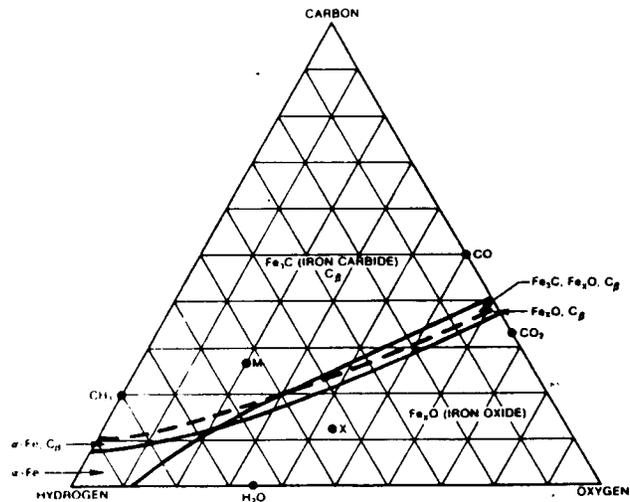


Figure 1. Phase diagram for the  $\alpha$ -Fe,  $Fe_xO$ ,  $Fe_3C$  and gas system.

checked with an on-line gas chromatograph. The iron samples used were number 2 steel wool, high purity  $\alpha$ -iron foil (>0.9999), and high purity  $\alpha$ -iron (>0.9999) vapor deposited on fused quartz. Most experiments were run by first bringing the  $\alpha$ -iron sample up to reaction temperature in pure hydrogen. Then the sample was either preconditioned (oxidized, carbonized, etc.) or was put directly under the gas composition of interest (i.e., in the phase field of interest).

## Results and Discussion

The results selected for presentation represent only a small fraction of the work done in this area by the author using this methodology. Also, it should be noted that others have used similar methodologies<sup>1,2</sup>.

Figure 2 represents a series of runs at various O/H values<sup>3</sup>. The gas phase compositions were adjusted to vary from a carbiding potential (cementite) to an oxidizing potential. Always carbon was thermodynamically favored to form. As illustrated, in the region where  $Fe_3O_4$  (magnetite) was the stable iron phase no weight gain was observed. In the cementite phase field weight gain

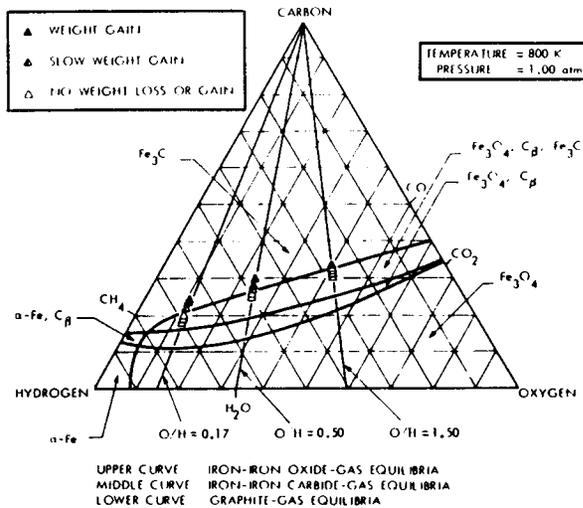


Figure 2. Inhibition of carbon deposition by  $Fe_3O_4$  at various O/H ratios.

was observed. Microscopic examination of the sample after reaction indicated this weight gain was carbon. A similar set of experiments is illustrated in Figure 3<sup>4</sup>. Again, cementite promotes carbon deposition. However, as shown, even though carbon is favored to form in the reduced iron phase field none does. Although not shown  $Fe_xO$  (wustite) and  $Fe_2O_3$  (hematite) also were shown not to support carbon deposition. Using this experimental strategy it is possible to investigate "individual" reaction as well. As presented in Figure 4 various mixtures of CO/CO<sub>2</sub> were exposed to a precarboned iron sample<sup>5</sup>. The CO concentration during all experiments favor carbon deposition from reaction 1



However, if the  $PCO/PCO_2$  ratio was less than or equal to 1.13 the surface will oxidize by reaction 2

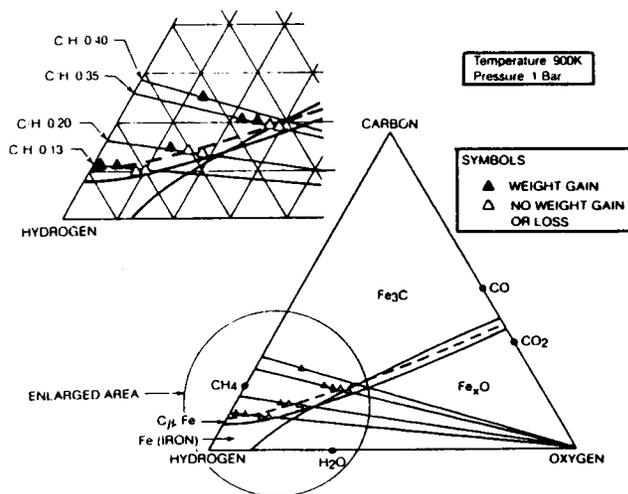
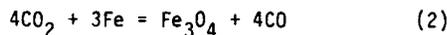


Figure 3. Evidence that cementite catalyzes carbon formation.

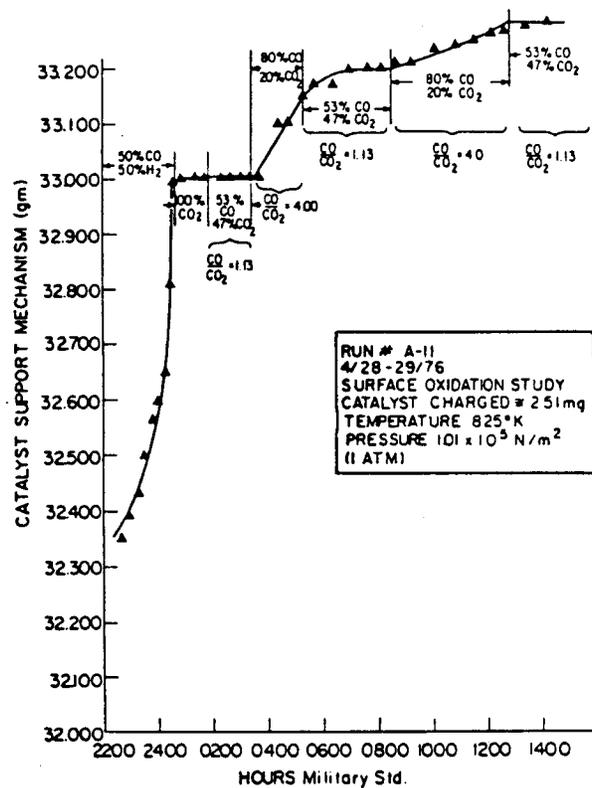


Figure 4. Effects of oxide inhibition in binary gas mixtures of Co-O<sub>2</sub>.

Notice that carbon deposition only occurred when reaction 2 was forced to the left. In other words, again iron oxide did not support carbon deposition. It should be pointed out that as long as the  $PCO/PCO_2$  ratio exceeds 0.23 the reduced surface will carbide to  $Fe_3C$ . This is the case in all experiments presented in Figure 4. These data are in agreement with all previous data, and illustrate how non-equilibrium phase diagrams can be used to elucidate complex heterogeneous catalytic systems.

#### Acknowledgement

The author thanks the National Aeronautics and Space Administration and the National Science Foundation for their help and support in all this work.

#### References

1. M.P. Manning and R.C. Reid, "C-H-O Systems in the Presence of an Iron Catalyst", *Ind. Eng. Chem. Process Design Develop.*, **16**, No. 3 (1977).
2. M. Audier, M. Coulon, and L. Bonnetain, "Disproportionation of CO on Iron-Cobalt Alloys - I Thermodynamic Study", *Carbon*, **21**, 93 (1983).
3. A. Sacco, Jr., and R.C. Reid, "Water Limitation in the C-H-O System Over Iron", *AIChE J.*, **25**, No. 5 (1979).
4. A. Sacco, Jr., and J. Caulmare, "Preliminary Results in the Investigation of the Growth and Initiation Mechanism of Filamentous Coke", *Adv. Chem. Series*, **202**, p. 177-191, ACS, Washington, DC (1982).
5. A. Sacco, Jr., "An Investigation of the Reactions of Carbon Dioxide, Carbon Monoxide, Methane, Hydrogen, and Water over Iron, Iron Carbides, and Iron Oxides", Ph.D. Thesis, Mass. Inst. Technol., Cambridge (1977).