

KINETICS OF THE GASIFICATION BY OXYGEN OF A GRAPHITIZING CARBON CATALYZED BY TRANSITION METAL IMPURITIES

H. Marsh, D.W. Taylor

Northern Carbon Research Laboratories, School of Chemistry,
The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, U.K.

Introduction

In a previous communication (Ref. 1) we discussed variations in the kinetics of gasification by molecular oxygen, as a function of the heat-treatment temperature (in the range 1200 K to 3200 K) of a graphitizing carbon prepared from polyvinyl acetate (PVA). The results of that study showed that with the samples of lowest HTT (1200 K to 1800 K) the reaction is catalyzed by the presence of residual hydrogen in the carbon. This is manifest by significantly higher rates of reaction (one to two orders of magnitude higher than for the PVA carbon, HTT 3200 K, depending on the HTT and the reaction temperature) and lower activation energies for the reaction (126 kJ mol⁻¹ for PVA 1200 K; 240 kJ mol⁻¹ for PVA 3200 K). This paper is concerned with an extension of these studies in which the effect is investigated on the reaction with oxygen of incorporating transition metal impurities (which are generally known to catalyze the carbon-oxygen reaction) into these anisotropic PVA carbons of HTT 1200 K.

The Experimental Approach

The 'pure' polyvinyl acetate carbon, HTT 1200 K, was prepared according to the method described previously (Ref. 1). Carbons doped with transition metals were prepared by dissolving a coordination compound (with the acetylacetonate ion) of the appropriate metal (e.g. for iron, Fe(C₅H₇O₂)₃) in the vinyl acetate, prior to polymerization and subsequent carbonization (to a final temperature of 1200 K heating at a rate of 5 K min⁻¹). This method of incorporation of metal into carbon is known (Ref. 2) to lead to a very fine dispersion of metal particles (~3-100 nm in diameter) distributed evenly through the carbon. The metal concentrations of the carbons studied (expressed as p.p.m. on an atomic basis i.e. number of metal atoms per 10⁶ carbon atoms) as determined by atomic absorption, are summarized in Table 1.

Table 1
Metal content of doped PVA 1200 K carbons (p.p.m.)

Metal added	Sample series		
	A (7 p.p.m. in polymer)	B (20 p.p.m.)	C (200 p.p.m.)
V	-	160	-
Cr	-	~300	-
Mn	-	520	-
Fe	-	105	-
Co	55	235	3150

Rates of gasification were measured gravimetrically (under conditions where the reaction rate is controlled by chemical processes only) by a vacuum microbalance (C.I. Electronics Mk. 2B; sensitivity $\pm 4 \mu\text{g}$), following outgassing for 3 hours at 1150 K,

on 50 mg samples of the carbon at an oxygen pressure of 1.33 kPa (10 torr). Further details of the experimental procedure can be found in reference 1.

Results

The kinetic results for the metal-doped carbons gave linear Arrhenius plots. The corresponding activation energies for the reaction are in Table 2.

Table 2
Activation Energy (E) for C-O₂ reaction (kJ mol⁻¹)

Metal added	Sample series		
	A	B	C
V	-	126	-
Cr	-	119	-
Mn	-	142	-
Fe	-	126	-
Co	157	141	148

cf for 'pure' PVA 1200 K sample E=126 kJ mol⁻¹

Discussion

One of the principal features of the results of Tables 1 and 2 is that three of the five metals studied (V, Co, and Fe), apparently do not influence the activation energy of the reaction of oxygen with these anisotropic carbons to any appreciable extent when compared with the undoped carbon of HTT 1200 K (E = 126 kJ mol⁻¹), although with chromium there is a small reduction to 119 kJ mol⁻¹. The reaction of oxygen with carbons doped with manganese proceeds with a higher activation energy (142 kJ mol⁻¹) than that of reaction with pure carbons. Also the rates of oxidation are not changed as dramatically as observed in other metal-carbon systems (Ref. 3). With the manganese-doped carbons the rate, compared to pure carbon, is only about 2.5 times faster. This is a rather unexpected result, perhaps associated with the use of a high density, anisotropic carbon of low surface area and almost total lack of internal porosity.

The cobalt-doped carbons are much more reactive than those carbons doped with comparable amounts of the other metals. The data in Table 3 show the temperatures which would correspond to rates of gasification of $1 \times 10^{-6} \text{ s}^{-1}$. Again, the reaction proceeds with an increased energy of activation for the three carbons doped with different concentrations of cobalt. Rates of reaction are enhanced however, by factors between 10² and 10³ more in keeping with previous experience (Ref. 3).

A possible explanation for inactivity in the present case is felt to be associated with the mode of dispersion of the metal within the carbons.

Table 3

Carbon		Temperature/K
Pure:		805
Cr	300 p.p.m.	794
Fe	105 p.p.m.	779
V	160 p.p.m.	775
Mn	520 p.p.m.	775
Co	55 p.p.m.	754
Co	235 p.p.m.	703
Co	3150 p.p.m.	648

It has already been mentioned that in these samples the metal is present as a very fine dispersion of particles distributed throughout the bulk of the material. In such circumstances only a very small fraction of the metal can be present at the surface of the carbon and therefore able to catalyze the reaction via the currently favoured oxygen-transfer mechanism (Ref. 3, 4). By contrast, most previous work has involved addition of the catalyst by direct deposition on to the carbon surface, or has used carbons of high internal surface areas.

Overall, the metal additions to these anisotropic carbons produce similar effects, differences being one of extent. Either the activation energy is unchanged or it is increased. Each of the metal additions produces a positive catalytic effect. The rates are not enhanced spectacularly except for those resulting from the additions of cobalt.

To understand this aspect of catalytic gasification, the exact state of dispersion of the metals in these carbons will have to be ascertained. It is still an open question if there has to be a minimum size of crystallite of metal or metal oxide before such a unit can become an effective catalyst. Also, if the efficiency of agglomeration of the metal in the carbon is high, there may be only a few effective units of catalyst available to the oxidizing gas. Cobalt may form suitably sized units. The other metals could be either too small or too big.

It could be suggested that the cobalt, in these partially graphitic anisotropic carbons, is able to catalyze the reaction via the alternative electron-transfer mechanism (Ref. 5) but this is difficult to prove.

The enhanced rates of oxidation, apparently, are brought about by the enhanced values of the pre-exponential values of the Arrhenius equation, rather than by a lowering of activation energies.

References

1. Taylor D.W. and Marsh H.
Carbon '76. Deutsche Keramische Gesellschaft
pp. 101-104 (1976).
2. Crawford D., Marsh H. and Taylor D.W.,
Carbon '76. Deutsche Keramische Gesellschaft.
pp. 243-246. (1976).
3. Walker P.L., Shelef M. and Anderson R.A.,
"Chemistry and Physics of Carbon", 4, 287 (1968).

4. McKee D.W.,
Carbon 8, 131 (1970); 13, 381 (1975).

5. Long F.J. and Sykes K.W.,
Proc. Roy. Soc., (London) A215, 100 (1952).

Acknowledgements

We express our thanks to the British Carbonization Research Association for financial support (H.M.) and a Research Fellowship (D.T.).