NITROGEN-DOPED CARBON-13 MATERIALS AS MODELS FOR THE STUDY OF NO_x AND N_2O RELEASE DURING COAL CHAR COMBUSTION

J.M. Jones and K. M. Thomas

Northern Carbon Research Laboratories, Department of Chemistry, Bedson Building, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, England.

INTRODUCTION

The release of nitrogen oxides into the atmosphere as a result of coal combustion is a major environmental problem. Therefore, there is a great deal of interest in determining factors which govern the release of gases such as NO_x and N_2O, over N_2, during coal and char combustion. One approach to studying the release of nitrogen from the char is to use model carbons with controlled heteroatom content and well-defined functionalities[1,2]. Previously we have demonstrated the potential of using isotopically-pure carbon-13 materials as model coal chars[3,4]. In this manner, N_2O and CO_2, and N_2 and CO, could be mass resolved and therefore the formation of these species could be followed by thermogravimetric analysis - mass spectrometry (TG-MS). It was found[3] that introducing nitrogen into the carbon by ammonia treatment resulted in the release of substantial amounts of N_2O during combustion.

The present work examines the role of structural characteristics and heteroatom content in the model carbons on their combustion characteristics, in particular the formation of nitrogen species.

EXPERIMENTAL

The carbon-13 starting materials were supplied by Aldrich Chemical Company. Model chars were produced by two different methods. Method one involved heat treating the sample under flowing argon (samples given the suffix -Ar), while method two involved heat treating the sample in flowing ammonia, either throughout the heating cycle (suffix -N) or only at the final heat-treatment temperature (suffix -Ar-N).

The temperature programmed combustion and desorption experiments were carried out in a Thermal Sciences STA 1500 thermogravimetric analyser. The model char sample (approx. 5 mg) was heated at 15 $Kmin^{-1}$ in the appropriate gas flow, i.e. 20% or 5% O_2/Ar for combustion and argon for desorption). The evolved gases were sampled at a height of approximately 1 cm above the surface of the sample by means of a heated silica capillary which connected the TGA instrument to a mass spectrometer.

RESULTS AND DISCUSSION

The analytical data for the samples used in this study are given in Table 1. The three different carbon batches obtained from Aldrich had quite different heteroatom content. This enabled the effect of heteroatom content on the combustion characteristics to be probed.

Table 1: Analytical data for the treated carbons

Samples	C wt%	H wt%	N wt%	O wt%
A-Ar	99.7	-	-	0.1
A-Ar-N	99.7	-	-	0.1
B-Ar	96.7	0.2	0.1	0.2
B-Ar-N	96.4	0.2	0.3	0.8
C-Ar	95.8	-	1.0	2.1
C-Ar-N	92.0	0.1	2.3	3.4
C-Ar(2)	95.9	-	0.6	nm*
C-N	93.1	0.2	1.7	nm*

*nm: not measured

The CO_2 temperature programmed gas evolution profiles had only one peak, the position of which moved to lower temperature as the oxygen content of the sample increased. The peak maxima of the CO evolution profiles occurred at lower temperatures than the respective CO_2 evolution profiles. For all samples peaks at m/z 28, 30 and 44 were detected. In addition to N_2 and N_2O, there will also be contributions to the m/z 28 and 44 profiles from ^{12}CO and $^{12}CO_2$ respectively because of the small amount of carbon-12 in the samples. However, in contrast to the CO and CO_2 profiles, the gas evolution profiles of the m/z 28, 30 and 44 were bimodal in nature. The two peaks were even more clearly resolved when the samples were combusted in 5% O_2/Ar. This is demonstrated for sample B-Ar-N in Figure 1.

The effect of the ammonia treatment is demonstrated in Figure 2. The potential problem of unresolved contributions of products with the same nominal mass, for example N_2O and $^{12}CO_2$ at m/z 44, can be estimated by assuming the Ar treated carbons provide "background" gas evolution profiles; i.e. by subtracting the peak areas of the Ar-treated samples from those of the corresponding ammonia-treated samples, the effect of ammonia treatment on the combustion characteristics was obtained.

These adjusted peak areas, dA, dB and dC indicated that the combustion behaviour of sample C was quite different to those of samples A and B: For samples A and B, N_2O was the major combustion product, and for sample C N_2 was the major combustion product. This difference may be related to a number of factors such as (i) temperature of combustion, (ii) oxygen content of the sample and (iii) nitrogen content or functionality of the sample.

Nitric oxide is considered to be the primary product of char-N oxidation, but this may react further in the pores and on the carbon surface. Clearly, the formation of N_2 and N_2O imply the existence of at least one mobile surface nitrogen complex. The relative amounts of N_2 and N_2O formed are unlikely to be due simply to the types of N-functionality in the carbons, although this is expected to have an impact. Rather they will have a complex relationship depending upon factors such as temperature, rate of combustion and concentration of surface nitrogen species. All these factors will influence the rates of reactions such as (i) desorption of C(NO) or C(N) surface species to form NO or N_2, (ii) reaction of $C(NO)_m$ and C(N) to form N_2O, (iii) reaction of N_2O with carbon.

CONCLUSIONS

The incorporation of nitrogen into carbon-13 materials is strongly influenced by the structure of the carbon. The highest amounts of nitrogen are incorporated when the carbon is highly reactive and possesses a high heteroatom content. This supports the proposal that NH_2 and NH radicals react with oxygen functionalities in the carbon[5]. The combustion products of the temperature programmed combustion of ammonia treated carbon samples include NO, N_2O and N_2. Each of these gases have bimodal evolution profiles suggesting the presence of two distinct nitrogen functionalities. The relative distribution of nitrogen in the carbon between these three products is dependent on the original precursor carbon; N_2 being a major product of NH_3-treated, high-oxygen content carbon. The relative amounts of N_2, N_2O and NO formed during combustion appears to have a complex dependence upon temperature of combustion, reactivity, oxygen content and nitrogen content and functionality in the carbon.

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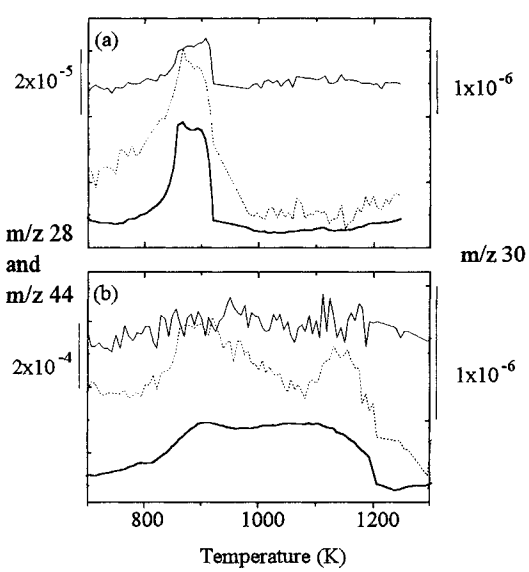

Figure 1: Gas evolution profiles of nitrogen species during the combustion of B-Ar-N in (a) 20% O_2/Ar and (b) 5% O_2/Ar. —— m/z 28, ▬▬ m/z 44 and ..... m/z 30

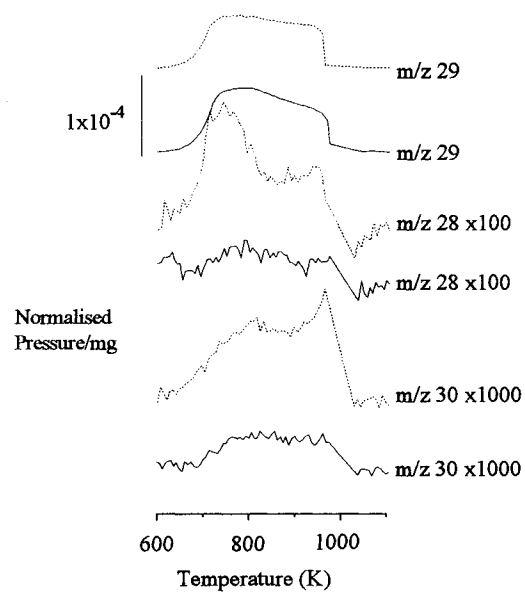

Figure 2: Comparison of evolved gas profiles during the combustion of C-Ar (——) and C-Ar-N(.....) in 5% O_2/Ar.