

Effect of Iron on the Evolution of Nitrogen Species During the Combustion of Model Carbons

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Introduction

NO_x emission from coal combustion has a major impact on the environment[1]. In the case of low-NO_x burners, char nitrogen is the major contributor to the NO_x formed. Therefore, the conversion of char nitrogen to NO_x during coal combustion/gasification is of considerable interest from an environmental perspective.

It is known that many metals or their oxides catalyse carbon gasification[2]. The influence of metallic particles on the gasification of pure graphite has received intensive investigation and the basic mechanism is understood. However their influence on the gasification/combustion of disordered carbons encountered in carbonaceous systems of commercial interest is much less understood. The influence of catalysts on NO_x emission during coal combustion has received little attention. However a difficulty arises in the study of naturally occurring carbon precursors such as coal because of the wide variety and heterogeneous distribution of the inorganic species, which affect the combustion/gasification behaviour of the carbon. As a consequence a suite of model carbons was used in the study. This study involved an investigation of the influence of iron catalysts on the behaviour of model carbon gasification/combustion and of nitrogen release from carbon combustion.

Experimental

Acenaphthylene, PVDC and alnovol resin were carbonised under an atmosphere of argon at 873 K and atmospheric pressure. The resulting carbons were ground and sieved to a particle size 38~75 μm. The carbons obtained underwent heat treatment either in argon or in ammonia, to a HTT of 1073 K. Iron was added to the carbons by impregnation using a solution of Iron(II) acetate. The concentration and amount of the solution were chosen so to give each carbon a metal loading of 1 wt. %.

The C, H, N and O contents of the carbons were obtained by using Carlo Erba Elemental Analyser. The total surface areas (TSA) of the carbons were determined using a McBain spring rig to obtain the adsorption isotherm of CO₂ at 273 K. The reactivities of the carbons in air were measured using a thermogravimetric analyser. Their

temperature programmed combustion (TPC) gas evolution profiles in 20% oxygen/argon were obtained using a thermogravimetric-mass spectrometer (TGMS). The heating rate of TPC was 15 K/min..

Results and discussion

When the pure carbons were treated in ammonia, up to 6~8 wt. % nitrogen was incorporated into the carbon structure. However, the ammonia treatment introduced only ~2 wt. % nitrogen into the iron containing carbons. The TSA of the carbons decreased after iron impregnation. These are indicative of the blockage of the micropores by the iron particles and their probable interaction in the nitrogen incorporation process.

Adding iron had an apparent promotional effect on the oxidation reactivity of the anisotropic acenaphthylene carbons, while adding iron to isotropic PVDC and resin carbons gave only a small increase in their reactivity. The pure acenaphthylene carbon is much less reactive compared with PVDC and resin carbon. When iron catalysts are present, the reactivity of acenaphthylene carbons is increased significantly but is still slightly lower than the corresponding PVDC and resin carbons.

The TPC gas evolution profiles of pure acenaphthylene, PVDC and resin carbons have been investigated previously[3, 4]. The general feature of the profiles is that the formation of CO reaches a maximum rate before CO₂, the release of NO is always delayed relative to CO₂ and reaches a maximum rate in the final stage of combustion. In the case of acenaphthylene carbon, there is evidence that two sites with different reactivity exist in the carbon structure. The ammonia treatment resulted in clearly bimodal TPC gas evolution profiles[3]. When iron catalysts are present in the carbon, the bimodal profiles were no longer observed. Instead, CO, CO₂ and NO were evolved together and reached a maximum rate at the same temperature (Fig. 1A & B). This suggests that during iron catalysed combustion of acenaphthylene carbons, catalytic effects were observed. The reactivity of the carbon sites no longer dominated the carbon combustion rate. Instead the reactivity at the catalyst-carbon interface determined the combustion process.

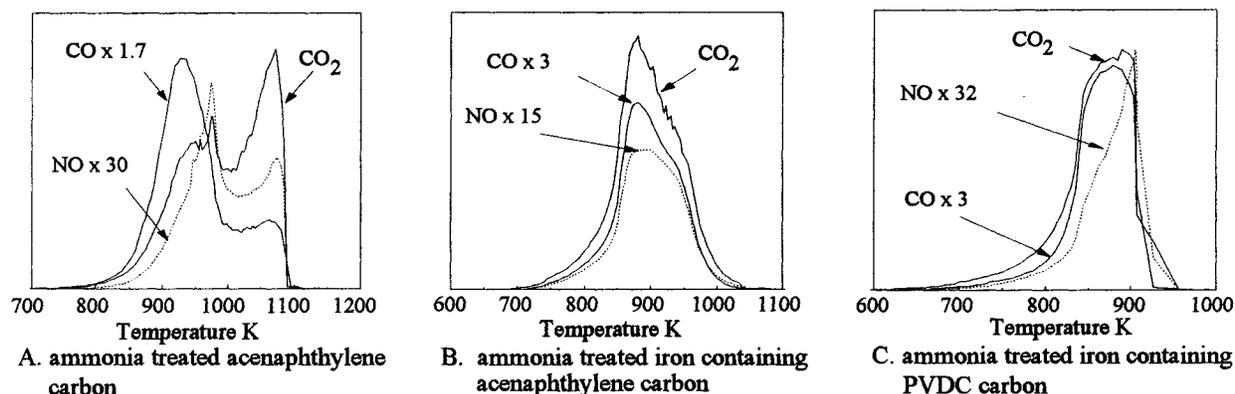


Fig. 1 Gas evolution profiles of temperature programmed combustion

The iron had a modified effect on the isotropic carbons. For both PVDC and resin carbons, the TPC gas release profiles of CO and CO₂ followed each other, as found with acenaphthylene carbon. The NO release was still delayed with respect to CO and CO₂ (Fig. 1C) but to a lesser degree than for the corresponding iron free carbon. The PVDC and resin carbons are very reactive. At the temperature when the iron catalysts became active, some of the carbon sites were also reactive. It is likely that the catalytic attack and uncatalysed oxidation took place simultaneously during combustion.

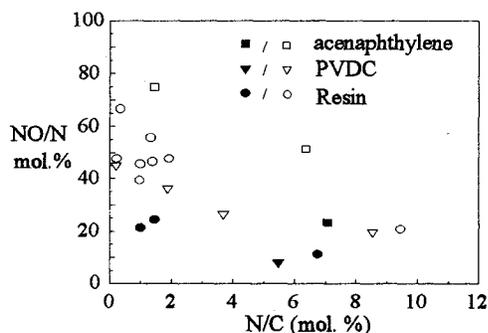


Fig. 2 Char nitrogen conversion to NO during TPC
open symbols — Fe doped carbons
filled symbols — pure carbons

NO is the primary product of char nitrogen oxidation during carbon combustion. The NO formed is partly reduced to N₂ on the carbon surface. In this study, N₂ release during TPC could not be monitored because its m/z value (=28) coincides with that of CO. The conversion of nitrogen in the carbons during TPC to NO, that is NO/N ratios, are in the range of 20 ~ 80%. In general, the iron containing carbons gave higher NO/N ratios than the corresponding pure carbons (Fig. 2). This

can be explained by the iron catalysts modifying the carbon sites and concentration of oxygen surface complexes resulting in a decrease in the NO reduction during TPC.

Conclusions

The catalytic effect of iron on carbon combustion has been observed but it is not as an effective catalyst for isotropic PVDC and resin carbon compared with anisotropic acenaphthylene carbon. The iron catalysed combustion results in the TPC CO, CO₂ and NO evolution profile maxima being observed closer together in temperature. The iron catalysts inhibit NO reduction in the pores and on the carbon active sites resulting in a higher char nitrogen conversion to NO. The iron catalysts also appear to hinder the introduction of nitrogen into the carbons by ammonia treatment.

References

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