

FLOW INJECTION - THERMAL GRAVIMETRIC ANALYSIS - MASS SPECTROMETRY: APPLICATION TO CARBON COMBUSTION/GASIFICATION

K. M. Thomas and J. M. Jones

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

INTRODUCTION

Detection of low concentrations of the types of short-lived species proposed as intermediates in the formation of NO_x and SO_2 during coal and coal char combustion presents a difficult analytical problem. Much of the information regarding the mechanism of NO_x and SO_2 release has been obtained from the study of homogeneous gas phase reactions of hydrocarbon flame species. Analysis of flame species has been conducted using optical spectrometry or probe sampling with mass spectrometric detection[1]. Mass spectrometry allows, at least in principle, the detection of all flame species. Molecular beam sampling of low pressure flames has allowed these studies to be carried out with high spatial resolution[2].

In the study of coal or char combustion, analysis of evolved gases by mass spectrometry is not simple because of the presence of a number of species with the same nominal mass. However, model coal chars derived from $> 99\%$ ^{13}C have been useful for studying the release of N_2 , N_2O and NO during combustion[3,4]. Also, we have demonstrated the usefulness of thermogravimetric analysis - mass spectrometry (TG-MS) with direct sampling of the gas phase close to the sample surface for the detection of reactive intermediate species during coal char combustion. The present work discusses a modification of this technique which has proved valuable for probing both homogeneous gas phase, and heterogeneous surface reactions *in situ* by mass spectrometry.

EXPERIMENTAL

Reactant gases were injected into the argon flow at the entrance to the TGA furnace (Stanton Redcroft 1500) using World Precision Instrument SP200 Series syringe pumps and SGE gas-tight syringes. The evolved gases were probed by means of a heated capillary line at a height of approximately 1 cm above the surface of the sample, and monitored by mass spectrometry. Sampling gases at the exhaust of the TGA was also possible by means of the second capillary. Up to fifteen different species could be monitored simultaneously.

RESULTS AND DISCUSSION

This technique allows injection response profiles to be generated and surfaces to be doped with surface species prior to reaction with specific gases. Furthermore, the small quantities of gas used in the injection studies enables isotopic substitution experiments to be carried out in a cost effective manner. A number of investigations are underway using the technique of flow-injection thermogravimetric analysis - mass spectrometry (FITGAMS). Some of the results are presented here in order to highlight some of the applications.

The carbon/NO reaction

Figure 1 shows some of the results obtained when NO was injected over an ammonia-treated carbon-13 model

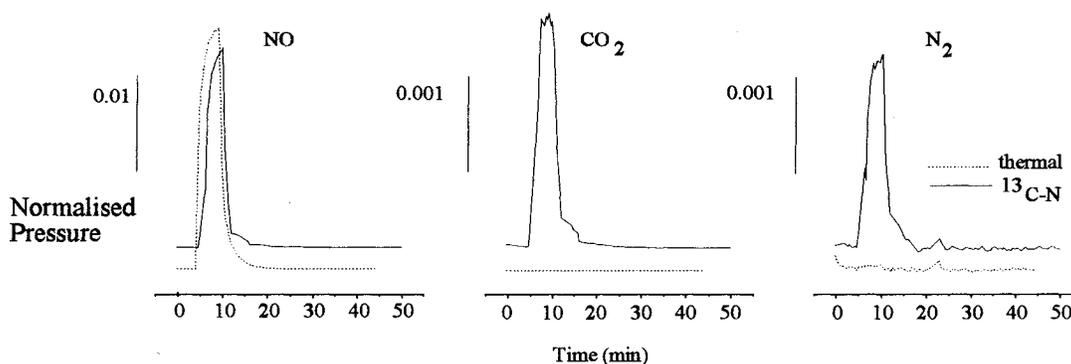


Fig. 1: Evolved gas profiles during FITGAMS of NO (25.0 ml injected at 5.0 ml min^{-1}) over no sample, and a nitrogen-doped carbon-13 sample ($^{13}\text{C-N}$).

char at 700 °C. Peak areas were reproducible with an error of < 1%. It is clear from Figure 1 that thermal decomposition of NO does not occur appreciably at this temperature. However, substantial reaction of NO with the model char is seen to occur. N₂ (m/z 28), ¹³CO (m/z 29), ¹³CO₂ (m/z 45) and possibly small amounts of N₂O (m/z 44) are observed.

The NO+NH₃ reaction

Figure 2 gives some preliminary findings of this study. It is intended to extend this work to investigate the selective catalytic reduction of NO by NH₃ over carbon catalysts. Gas evolution profiles are shown for m/z 28, 18, 2 and 44 corresponding to N₂, H₂O, H₂ and N₂O. Injections of ammonia only, nitric oxide only, and simultaneous injection of ammonia and nitric oxide were made at 400 °C. Examination of the m/z 28 and 18 profiles indicate that the reduction of NO by NH₃ to form N₂ and H₂O occurs thermally at this temperature. It is interesting to note that more water is formed for injection of ammonia over ¹³C-N compared to that formed thermally. This suggests that the reaction of NH₃ or C(H)₁ with surface oxide species (C(O)) is occurring.

Peaks at m/z 2 are observed when injections of NH₃ are made, showing that thermal decomposition of ammonia is also takes place. Finally, the large m/z 44 peak observed when NO and NH₃ are injected simultaneously suggests that NH₃ and NO react in the gas

phase to form N₂O and presumably H₂ and/or water.

No evidence of catalysis by the carbon was observed for reactions at this temperature and in the absence of oxygen. The carbon was reacting with the injected NO, however, and peaks due to ¹³CO and ¹³CO₂ were evident.

CONCLUSIONS

Flow injection - thermal gravimetric analysis - mass spectrometry (FITGAMS) has been shown to be a useful technique for probing complex heterogeneous char gasification reactions. Stepwise, or simultaneous, injection of different reactants means that the formation and reaction of surface species can be probed. The small amount of reactants required, and the ease of containment of materials, means that FITGAMS also lends itself to isotopic labelling studies.

REFERENCES

1. D.J. Seery and M.F. Zabielski, *Combustion and Flame* **78**, 169 (1989).
2. R. Harvey and A. Maccoll, *J. Chem. Soc. Faraday Trans. 1*, **75**, 2423 (1979).
3. K.M. Thomas, K. Grant and K. Tate, *Fuel* **72**, 941 (1993).
4. J.M. Jones and K. M. Thomas, *Carbon* (in press).
5. J.M. Jones, A.W. Harding, S.D. Brown and K.M. Thomas, *Carbon* (in press).

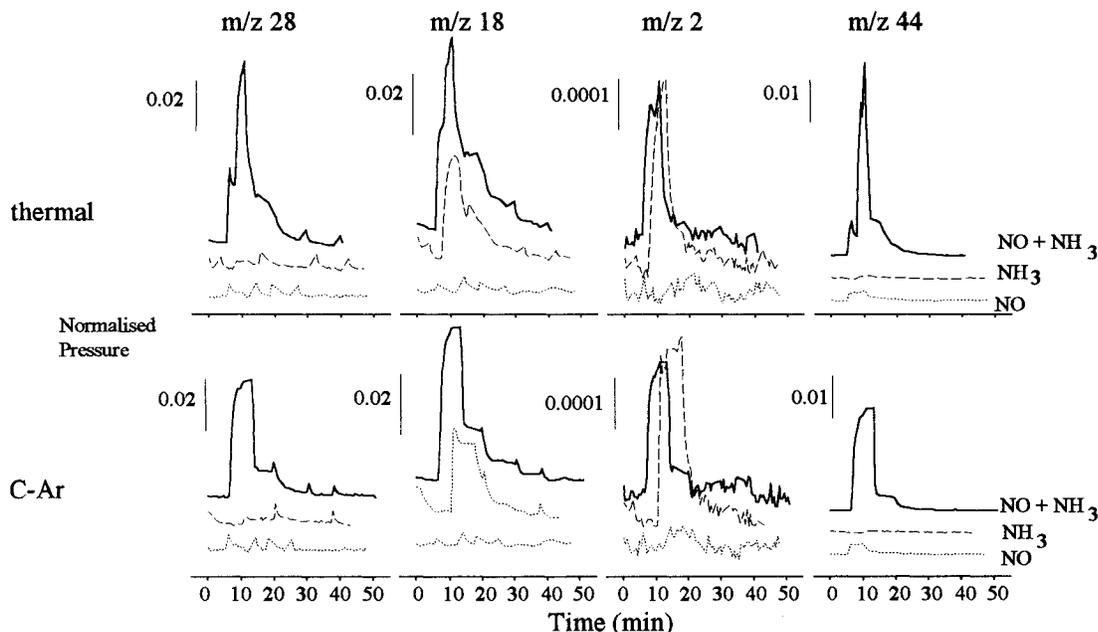


Fig. 2: Evolved gas profiles during FITGAMS of NO and/or NH₃ (25 ml at 5mlmin⁻¹) over (a) no sample (thermal) and (b) carbon-13 (C-Ar) at 400 °C.