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TG-MS FOR CHARACTERIZATION OF ACTIVATED CARBONS FROM COAL

By

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INTRODUCTION

The application of thermogravimetry coupled with a quadrupole mass spectrometer (TG-MS) to study coal-based materials was examined. First, TG-MS was used to analyze the gaseous decomposition products from activated coal-based carbons to obtain structural information related to their synthesis conditions. Secondly, adsorption/desorption profiles of physisorbed and chemisorbed gases were determined through temperature programmed desorption/evolved gas analysis (TPD/EGA).

There are a number of reviews on the use of TG-MS systems to study decomposition and kinetics of biological, organic, and inorganic compounds.^{1,2,3} This method has several advantages over other instrumentation used for TPD/EGA. For example, methods that utilize gas chromatography (GC) to monitor gas release are limited to only a few gases and the time required for each analysis results in discontinuous gas evolution profiles^{4,5}. Newer methods, which couple MS to the reactors used for TPD, provide a significant improvement; however many of these systems do not have continuous sample weight monitoring^{6,7}.

The TG-MS system used for this study provided the ability to accurately and continuously monitor weight changes simultaneously with evolved gas composition. The quadrupole MS system employed allows determination of multiple gas components in the range of 0-300 atomic mass units. Procedures for determining relative gas evolution rates and quantities have been developed. The system is equipped with multiple sweep and reaction gas purge, gas switching, and gas blending capabilities which make possible the study of adsorption and desorption of gases under a wide variety of conditions.

EXPERIMENTAL

Instrumentation

A Seiko TG/DTA 320 was coupled to a VG Micromass quadrupole MS. The TG was connected to a disk station which provided for programmable control of the furnace, continuous weight measurements, sweep gas valve switching, data analysis, and export of data to other computers. The TG has a temperature range of room temperature to

1300°C. The MS has a Nier type enclosed ion source, a triple mass filter, and two detectors (a Faraday cup and a secondary emissions multiplier). The MS was controlled by a dedicated personal computer which was also used to acquire and review scans before export to a spreadsheet for data manipulation.

The two instruments were coupled by a fused silica capillary transfer line leading from above the sample pan in the TG to an inert metrasil molecular leak which interfaced the capillary with the enclosed ion source of the MS. Connections at both ends of the capillary allowed sampling of very small fractions of the gases. The transfer line was heated to 170°C at which temperature the flow rate through the capillary was approximately 12 ml/min .

TG-MS procedures

The TG conditions used to study the relationship between the structure and synthesis parameters of carbons were: heating rate of 10°C/min to a 5 min hold at 900°C; sweep gas, 225 ml/min; constant sample volume weighing 10-25mg. The MS was scanned over a 0-100 amu range with measurement intervals of approximately 30 seconds.

The TG heating profile for TPD/EGA measurements was more complex and incorporated segments for outgassing, cooling, adsorption, desorption, and temperature-induced desorption (Table I). During outgassing and subsequent cooling of the sample to an adsorption temperature (segments a and b, Table I), an inert (He) gas sweep was usually used after which the gas to be adsorbed was introduced. After completion of an adsorption interval, He was again used to purge the system during segments d and e. Multiple and consecutive adsorption/desorption cycles were performed by recycling the temperature programmer to segment b.

The relative amounts of effluent gases monitored by the MS was determined using the He peak intensity, at a constant flow rate, to determine a sensitivity factor for each analysis. The area under the gas evolution curve for each gas was determined, normalized for the sample weight, and multiplied by the sensitivity factor obtained by arbitrarily assigning a value of one to the He intensity of one of the runs to be compared. This run was referred to as the standard run. The sensitivity factor was then calculated by dividing the He intensity of the standard run by the intensity of He in all subsequent runs. The intensities of all other gases of interest were multiplied by the sensitivity factor for relative comparisons.

Materials

Activated carbons produced by chemical and thermal procedures were studied during the first part of this work. They were produced from Illinois Basin bituminous coals supplied by the Illinois Basin Coal Sample Program and were prepared according to procedures detailed elsewhere^{8,9,10}. Two types of chemical activation were examined, H₃PO₄ and KOH. Temperature treatments were 170 and 500°C for acid treated carbons and 75, 400 and 800°C for base treated carbons. All carbons were leached to a pH of 7 and dried before TG-MS analysis.

During the TPD/EGA study, a commercially (Carbotech) produced coal-based

carbon was used. This carbon was produced by thermal activation and had a N₂ BET surface area of 450 m²/g. The adsorption gas mixture was 2% NO, 10% O₂, 15% CO₂ with He the balance.

RESULTS AND DISCUSSION

Structural determinations

TG-MS experimental data enables the correlation of weight loss to individual gas evolution. The temperature of evolution has been related to different functional groups on the surface of the carbon matrix¹¹. For example, the data in Figure 2 were from a carbon sample thermally treated at 500°C. Maxima in the evolution profiles for CH₄ and H₂ were at 620 and 820°C. Dealkylation is a likely source of the CH₄ release¹². H₂ and CH₄ evolution began at about the same temperature but H₂ continued to be evolved after CH₄ release had stopped. This suggests that H₂ from more than one source contributes to its evolution profile. Possible sources are the decomposition of aliphatics at lower temperatures and aromatics at higher temperatures¹². Very little CO₂ (mass 44) was evolved which suggests that the CO_x (mass 28) evolution profile represents primarily CO release. Presently work is being done to correlate these TG-MS CO and CO₂ evolution determinations to carbonyl and aromatic C-O measurements by FTIR.

No significant amounts of other gases were detected by MS. Gas identification was based on a comparison of several ions. For instance, the identification of CH₄ was based on a comparison of mass 16 with mass 32 (O₂). Mass 32 did not deviate significantly from barely detectable levels. In this example, weight loss cannot be assigned to a specific gas since evolution profiles overlap. However, weight loss corresponded well with the onset of gas evolution.

Important to this study was a comparison of the relative amount of gas evolved from carbons produced under different synthesis conditions. A number of factors (condition of the capillary transfer tube, the ion source, and the efficiency of the vacuum system) affect the sensitivity of the MS. Therefore, comparison of spectra required the development of a method to correct for the sensitivity of the MS. Helium was used as an internal standard to calculate a sensitivity correction factor for each spectra. Since the flow rate and concentration of He was held constant for each experiment and the amount of gases evolved from the sample was negligible in comparison to the concentration of He, each spectra was corrected to the same He intensity arbitrarily chosen from the spectra to be compared. Further, comparison of gases on a unit basis required normalization of the relative amount of gas evolved for the differing initial sample weights.

Using the above approach, carbons produced under a number of thermal, acid and base treatments were examined. H₂ and CH₄ evolution profiles were compared for three carbons treated as follows: low followed by high temperature treatment (170°C and 500°C); low followed by high temperature treatment with H₃PO₄; and high temperature treatment with acid (Figure 3 and 4). These three samples, though activated at the same maximum temperature, had quite different H₂ evolution profiles. The acid treatment appeared to remove more low temperature H₂ since evolution began at 460°C for the thermal only sample and at nearly 600°C for acid treated samples. Additionally, the

temperature of maximum H₂ evolution was shifted slightly higher for acid treated carbons. CH₄ evolution was observed only for the carbon sample that had a thermal treatment without acid. If the CH₄ results from the pyrolytic cleavage of aliphatic carbon side chain in the parent coal structure, then acid treatment promoted these dealkylation reactions. The calculated relative amounts of H₂ released indicated that acid treatment promotes dehydrogenation (Figure 3 and 5) during synthesis. The relative amounts of evolved H₂ were consistent with H/C atomic ratios calculated from elemental analysis of the carbons.

TG-MS data of four activated carbons produced under different thermal and base (KOH) treatments were also compared (Figure 6). The relative amount of evolved H₂ and CH₄ decreased with increased severity of treatment. The base activated carbon evolved substantially more CO and CO₂ than the thermal only treated sample. This is consistent with FTIR analyses of these samples which showed carbonyl group development in base treated samples which was not present in the parent coal⁹.

TPD/EGA determinations

The NO adsorption/desorption profiles (Figure 7) of a commercial coal-based activated carbon will be used as an example of a TPD/EGA determination performed by TG-MS. Adsorbing samples must be heated to a temperature as high as the maximum desorption temperature to remove any adsorbed gases. After this pre-conditioning step and sample cooling to 70°C, NO plus CO₂, O₂, and He were passed over the sample until its weight approached saturation. The NO was turned off and a He sweep gas was passed over the sample at the adsorption temperature for a period of time. This interval allowed purging of the NO from the system and removal of any physically bound NO from the carbon. The sample was then heated at 10°C/min to a maximum desorption temperature of 400°C. In Figure 7, some weight loss occurs during the low temperature desorption period but the MS spectrum showed an intense peak at mass 30 which correlated well with the weight loss during heating. The temperature at which maximum evolution occurred was 132°C. This temperature indicates NO is not strongly bound to the carbon matrix. The only gas evolved during desorption was NO which allows the direct correlation of weight loss with NO desorption. Any number of adsorption/desorption cycles can be consecutively run. The sample in Figure 6 was repeated three times.

SUMMARY AND CONCLUSIONS

TG-MS has been successfully applied to the study of coal-based activated carbons providing information which relates synthesis parameters to the structure of the carbons. Procedures were developed to compare the relative quantities of evolved gases. The instrumentation was also used to do TPD/EGA analyses of activated carbons. Their adsorption and desorption properties are important in evaluating the practical applications.

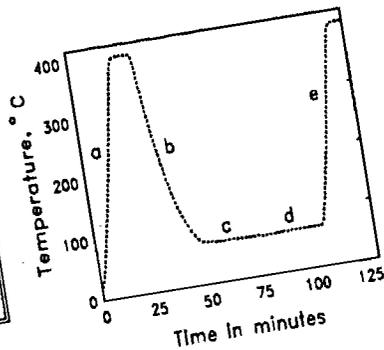
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Table I. TG heating profile for ADP.

Step	Temp C	Rate C/min	Hold min
a	0-400	20	10
b	400-70	50	10
c	70 (1)	0	60
d	70 (2)	0	30
e	70-400	20	10



¹Adsorption
²Low temperature desorption

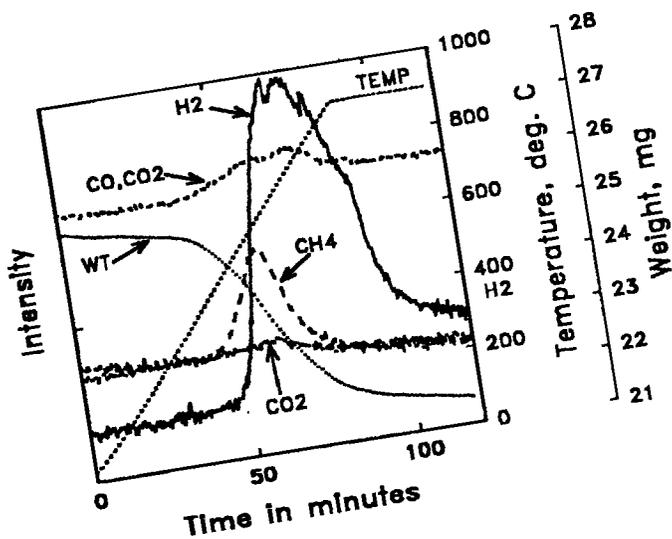


Figure 1. TG-MS analysis of thermally treated activated carbon from IBC sample.

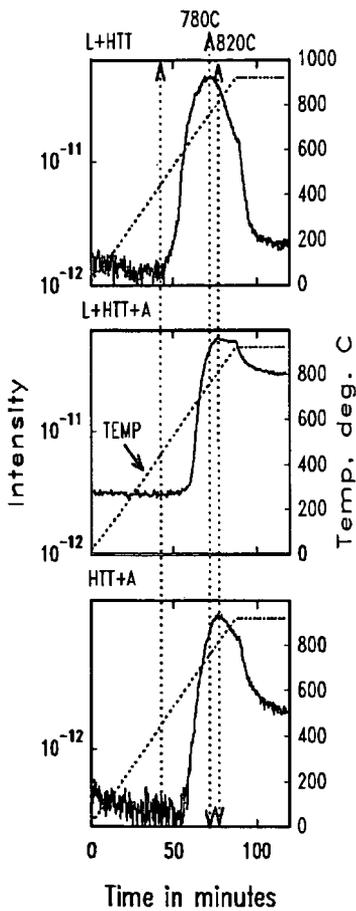


Figure 3. H₂ evolution curves from TG-MS analysis of acid and heat treated coal-based active carbons. A=H₃PO₄; L=low; HTT=high temperature treatment

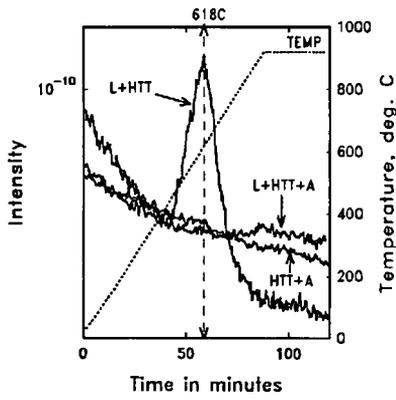


Figure 4. CH₄ evolutions curves from TG-MS analysis of acid and thermally activated coal-based carbons. A=H₃PO₄; L=low; HTT=high temperature treatment

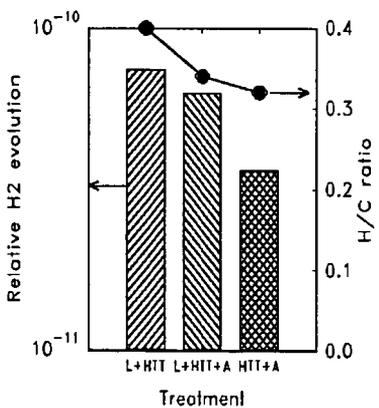


Figure 5. Relative amounts of H₂ evolved from acid and heat treated coal-based carbons. A=H₃PO₄; L=low; HTT=high temperature treatment

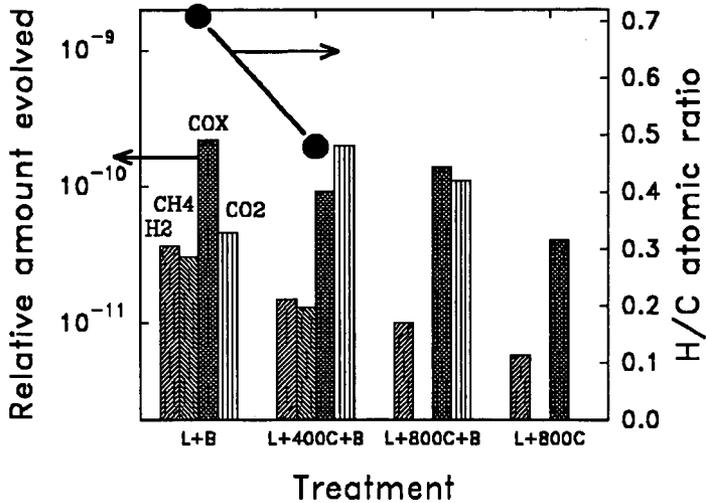


Figure 6. Relative amounts of H₂, CH₄, CO, CO₂ evolution from KOH activated carbons. B=KOH, L=low temperature treatment, 75°C

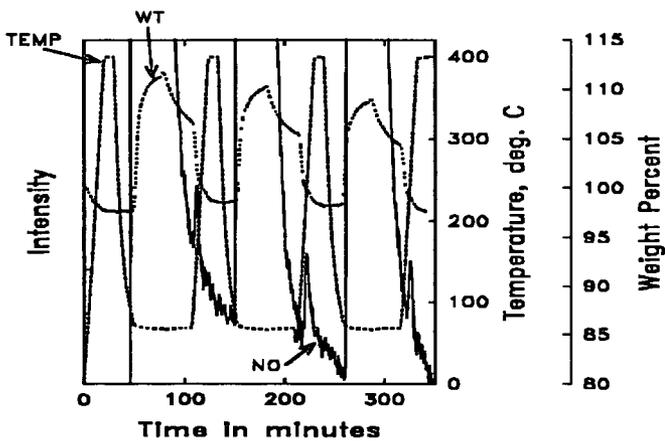


Figure 7. NO adsorption/desorption profile for coal-based activated carbon as determined by TG-MS.