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Evaluation of atmospheric solids analysis probe mass spectrometry for the analysis of coal-related model compounds

Shou-Ze Wang [a], Xing Fan [a,*], Ai-Li Zheng [a], Yu-Gao Wang [a], You-Quan Dou [a], Xian-Yong Wei [a], Yun-Peng Zhao [a], Rui-Yu Wang [b], Zhi-Min Zong [a], Wei Zhao [a]

[a] *School of Chemical Engineering, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China*
[b] *Low-Carbon Energy Institute, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China*

HIGHLIGHTS

- ASAP was applied to analyze CRMCs, exploring a new application field.
- The ionization mechanism of produced $M^{+\cdot}$ and $[M+H]^+$ for CRMCs were investigated.
- The ASAP/MS fragmentation pathways for selected CRMCs were proposed.

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ABSTRACT

An atmospheric pressure solids analysis probe (ASAP) was mounted on a commercial atmospheric pressure chemical ionization source with simple modifications. A series of coal-related model compounds (CRMCs) were analyzed using a time-of-flight mass spectrometry equipped with the ASAP ion source. The ionization mechanism and fragmentation pathways for CRMCs were investigated. The temperature of desolvation gas played a crucial role to the response signal, especially for the association behavior of CRMCs. With a fixed desolvation gas temperature, radical cation ($M^{+\cdot}$) or protonated molecule ($[M+H]^+$) was the predominant ion generated by corona discharge of ASAP depending on the temperature of drying gas. Fragment ions were produced from bridged bond breaking of the precursor ions, rearrangement reactions and loss of neutral fragments such as H_2O, CH_2O, CO, CH_3OH and CO_2. The fragmentation pathways can offer a better understanding of fundamental mechanism of chemical bond breaking for coal derivatives and further explore the application of coal directional conversion.

1. Introduction

As a fossil energy, coal can be utilized by combustion to generate heat. But coal processing is needed prior to combustion to reduce the emissions of gaseous pollutants such as SO_x and NO_x [1]. Coal has extremely complex structures and consists of a wide range of organic species [2]. To utilize coal in a clean and high efficient way, it is desirable to understand the detailed chemical composition of coal and how the composition varies during the process of coal conversion. Lots of efforts have been contributed to the characterization of coal structures and molecular composition in coals. Infrared spectroscopy is commonly applied to acquire the structural information of coals, especially nitrogen, sulfur and oxygen functionalities [3]. Using nuclear magnetic resonance (NMR), Cai et al. proved that the NMR transverse relaxation distributions of water saturated cores strongly related to the structure of coal pore and coal rank [4].

Mass spectrometry (MS) has been developed for characterizing components in coals and proved a powerful tool for the identification of unknown organic species [2,5]. Various MS ionization methods such as electron ionization (EI) [6], electrospray ionization (ESI) [7], atmospheric pressure photoionization (APPI) [8], and atmospheric pressure chemical ionization (APCI) [9] have been employed for the analysis of coal derivatives. However, results from MS analysis of coals and coal derivatives are too complicated to screen useful information for the studies on molecular association and directional conversion of organic species in coals. Coal-related model compounds (CRMCs) play an important role in understanding molecular association and directional conversion of molecules in coals, which can promote effective, clean and value-added utilization of coals [10–15]. It is necessary to elucidate the ionization mechanism and fragmentation pathways of various ionization techniques for CRMCs, which can be further applied to explaining the complex mass spectra for products of coal conversion.

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* Corresponding author. Tel.: +86 516 83885951; fax: +86 516 83884399.
E-mail address: fanxing@cumt.edu.cn (X. Fan).

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Ambient ionization for MS is a series of ionization techniques performed under open-air conditions [16]. Ambient ionization techniques such as desorption electrospray ionization (DESI) [17–20] and direct analysis in real time (DART) [20–23] have been widely employed in MS analysis due to the advantage that samples can be directly and rapidly analyzed with high throughput and minimal sample pretreatment. Coal derivatives have been successfully analyzed using ambient ionization MS, such as DART/MS [24]. Atmospheric solids analysis probe (ASAP) is also an ambient ionization technology that is derived from APCI with a few modifications [25]. Compared to APCI, liquid chromatography (LC) is not required for ASAP. Thus analyte that is not soluble in the mobile phase of LC can be directly analyzed using ASAP. The potential application of ASAP ion source coupling with MS (ASAP/MS) have been explored in various fields such as analysis of steroids [26], drugs [27,28], nucleosides [29], polymers [30,31], and chemicals in food [32]. However, there is no report on the structural characterization of coal derivatives or CRMCs using ASAP/MS. It is necessary to understand ionization mechanism and fragmentation pathways of CRMCs, such as bond breaking for methylene bridged linkages or heteroatom bridged bonds, in the corona discharge ionization of ASAP.

In this work, a series of CRMCs containing C, H and O atoms were analyzed using a time-of-flight MS (TOF-MS) equipped with an ASAP ion source. By regulating the parameters of ion source such as the temperature of nitrogen gas, radical cations, protonated molecules and fragment ions were acquired and compared. The corresponding fragmentation pathways were also discussed. These results offered a better understanding of the process of ion formation and chemical bond breaking of organic species in MS analysis of coal derivatives, which could further explore the fundamental mechanism for coal directional conversion.

2. Experimental

The CRMCs listed in Table 1 with >97% purity were obtained from Fluka Chemie GmbH, Germany, and analyzed using an ASAP (Model ASAP™, IonSense, USA) coupling with a TOF-MS (Model G6210; Agilent Technologies, USA). The configuration of ASAP derived from an APCI source is shown in Fig. 1. A melting point (mp) capillary with 25 mm length and 1.7 mm outer diameter was mounted on the center of an ASAP probe. Sample was dipped on the end of the mp capillary and introduced directly into the ion source with the ASAP probe. The mp capillary was baked in the ion source at 350 °C for at least 30 s prior to use to avoid any residual contamination on the surface of capillary. Sample was first vaporized by heated nitrogen gas from the heater, followed by ionization with electrical discharge near the corona needle.

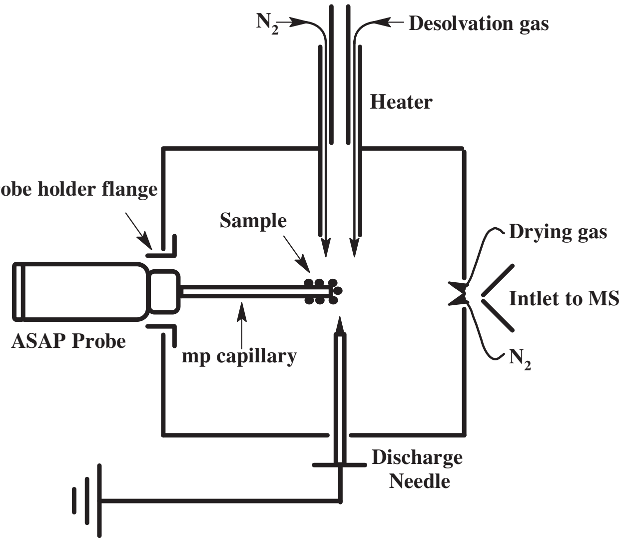

Fig. 1. The configuration of the ASAP source derived from APCI.

The ASAP source was operated in positive ion mode with a corona current of 4.0 μA and a capillary voltage of 4000 V. The nebulizer pressure was set to 40 psi and drying gas flow rate to 9 L min^{-1}. As shown in Fig. 1, two streams of nitrogen gas were introduced into the ASAP source housing: one from the heater called desolvation gas and the other one close to the inlet named drying gas. Typically, the temperature of desolvation gas was set in the range of 100–400 °C, and the drying gas temperature from 100 to 300 °C. In this work, the temperature of desolvation gas was optimized at 350 °C to acquire enough signal intensity and less associated ions, which will be discussed in the next section. To

Table 1
Molecular ions and fragment ions of the CRMCs obtained by ASAP/TOF-MS (structures of the CRMCs are listed in Supplementary data).

No.	Compound name	Molecular formula	Molecule weight	Ion		
				$M^{+\cdot}$	$[M+H]^+$	Fragment
1	Naphthalene	$C_{10}H_8$	128.17	128.06044[a]	Nd	
2	Anthracene	$C_{14}H_{10}$	178.23	178.07706	179.08728[a]	
3	Phenanthrene	$C_{14}H_{10}$	178.23	178.0737	179.08125[a]	
4	Pyrene	$C_{16}H_{10}$	202.25	203.07330	203.08158[a]	
5	Fluorene	$C_{13}H_{10}$	166.22	166.07556	167.08272[a]	
6	Acenaphthene	$C_{12}H_{10}$	154.21	154.07399	155.08153[a]	
7	1,3-Diphenylpropane	$C_{15}H_{16}$	196.29	196.12404[a]	197.12910	×
8	Triphenylmethane	$C_{19}H_{16}$	244.33	244.12165[a]	Nd	×
9	Triphenylethylene	$C_{20}H_{16}$	256.34	256.12199	257.12952[a]	×
10	9-Phenylanthracene	$C_{20}H_{14}$	254.33	254.10476	255.11294[a]	
11	9-Benzyl-*sym*-octahydroanthracene	$C_{21}H_{24}$	276.42	276.18326	277.19214[a]	×
12	Di(1-naphthyl)methane	$C_{21}H_{16}$	268.35	268.11932[a]	269.12521	×
13	1-(4-phenethylbenzyl)naphthalene	$C_{25}H_{22}$	322.44	322.16456[a]	323.17106	×
14	9,9′-Bifluorene	$C_{26}H_{18}$	330.42	330.13475	331.14314[a]	×
15	Hydroquinone	$C_6H_6O_2$	110.11	110.03458[a]	111.04166	
16	1-Naphthalenemethanol	$C_{11}H_{10}O$	158.20	158.06963[a]	159.07787	×
17	1-Naphthaldehyde	$C_{11}H_8O$	156.18	156.05404	157.06066[a]	×
18	1-Naphthoic acid	$C_{11}H_8O_2$	172.18	172.05012[a]	173.05836	×
19	2-Ethoxy-1,2-diphenylethanone	$C_{16}H_{16}O_2$	240.30	Nd	241.11820[a]	×
20	Dimethyl naphthalene-2,6-dicarboxylate	$C_{14}H_{12}O_4$	244.24	244.07079	245.07820[a]	×

[a] The predominant molecule ions; Nd = Not detected.