

Short communication

Tandem mass spectrometric evaluation of core structures of aromatic compounds after catalytic deoxygenation



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ABSTRACT

Catalytic deoxygenation of coal enhances the stability and combustion performance of coal-derived liquid fuels. However, determination of the selectivity of removal of oxygen atoms incorporated in or residing outside of aromatic rings is challenging. This limits the ability to evaluate the success of catalytic deoxygenation processes. A mass spectrometric method, in-source collision-activated dissociation (ISCAD), combined with high resolution product ion detection, is demonstrated to allow the determination of whether the oxygen atoms are in aromatic compounds reside outside of aromatic rings or part of the aromatic system, because alkyl chains can be removed from aromatic cores via ISCAD. Application of this method for the analysis of a subbituminous coal treated using a supported catalyst revealed that the catalytic treatment reduced the number of oxygen-containing heteroaromatic rings but not the number of oxygen atoms residing outside the aromatic rings.

1. Introduction

Alternative energy resources, such as coal-derived liquid fuels and shale crude oil, are of general interest due to the depletion of crude oil [1,2]. Coal liquefaction technology has drawn attention because of the large and widely distributed coal reserves compared to other hydrocarbonaceous sources [3]. However, the oxygen content in coal-derived liquids may exceed 10 wt% and is much higher than that of crude oil [4]. Reduction of the amount of organic oxygen in coal-derived liquids to the level present in crude oil will enhance the fuel stability and combustion performance [5].

In recent years, attempts to catalytically deoxygenate coals and coal derivatives have been reported [6–8]. Some organic oxygen in coal are present in the form of carbonyl, carboxyl, ether, hydroxy, and methoxy groups, but other organic oxygens are incorporated into heteroaromatic rings [9,10]. From previous studies on deoxygenation of model compounds, we propose three major catalytic deoxygenation pathways according to the position of oxygen in alkyl aromatics molecules, which are shown in Supplementary Data. Different catalytic processes are needed to remove organic oxygen located inside and outside aromatic rings [11,12]. Bulk elemental analysis is a direct way to determine the content of oxygen during coal conversion [13]. However, further details like the position of oxygen in molecules are still lacked, which limit the

evaluation of relationships between molecular structure and the corresponding reactivity. Therefore, the development of a method for the characterization of organic oxygen inside and outside aromatic rings is crucial for further understanding of the catalytic processes.

Identification of oxygen in alkyl groups or heteroaromatic rings can be realized by Fourier transform infrared spectroscopy [14], X-ray photoelectron spectroscopy [15], and nuclear magnetic resonance spectroscopy [16]. However, these analytical methods cannot reveal structural details of unknown oxygen-containing compounds in very complex mixtures. Mass spectrometry (MS) with high resolution has been employed to determine elemental compositions of compounds in liquid fuels and/or soluble portions generated from solid fuel resources [17–19]. In high-resolution mass spectrometry (HRMS), orbitrap MS has a higher resolving power than time-of-flight MS, and more affordable compared to Fourier transform ion cyclotron resonance MS. At the mean time, orbitrap MS is sufficient for adequate characterization of petroleum fractions under consideration [20]. However, the positions of oxygen and other heteroatoms inside or outside of aromatic rings of compounds in catalytically treated coals cannot be adequately differentiated by the above methodology. The in-source ion fragmentation method and HRMS have been employed in this work to evaluate aromatic core structures of compounds in coal fluids after catalytic deoxygenation.

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2. Experimental section

The coal sample, NiO/Mo₂O₃-ZSM-5 (catalyst) and cyclohexane (solvent) were mixed in an autoclave and allowed to react at 300 °C with hydrogen to obtain a coal filtrate (F1, 12.3 wt% of yield). A supported catalyst on ZSM-5 was reported to effectively crack the macromolecular network in coal under mild conditions (300 °C in cyclohexane) [21]. Details of the experiments are listed in Supplementary Data. The same experimental procedure was repeated without the catalyst to acquire another coal filtrate (F2, 8.2 wt% of yield). The results of bulk elemental analysis for F1 and F2 are listed in Table S4. Both filtrates were ready for the mass spectrometric characterization.

A high resolution linear quadrupole ion trap/orbitrap mass spectrometer (LTQ-Orbitrap XL, Thermo-Fisher Scientific, Waltham, USA), was used in the analytical work. The operation parameters of MS are also listed in Supplementary Data. Extractable components in the mass range from 50 up to 1000 Da were analyzed. In-source collision-activated dissociation (ISCAD) was realized at a collision energy of 100 V. Thermo Xcalibur Roadmap software Data Analysis 2.2 was used for peak selection and molecular formula assignment.

3. Results and discussion

Atmospheric pressure chemical ionization (APCI) and carbon disulfide as the ionization reagent have been demonstrated to efficiently ionize aromatic compounds, generating only stable molecular ions and no or minor fragment ions [22]. Therefore, this method is suitable for the analyses of soluble portions from coal that predominately contain alkyl aromatic compounds. High-resolution mass spectra were recorded for the ionized compounds to determine their elemental compositions. Soluble components in the cyclohexane filtrates with mass range from 50 up to 1000 Da were analyzed. Zoom insets of the mass spectra from HRMS have been introduced to offer evidences of the data quality and the sample complexity [23]. In this work, a mass scale-expansion of orbitrap mass spectra for soluble fractions without and with catalytic deoxygenation near 272 Da was provided in Fig. 1. After catalytic treatment, the relative abundances of oxygen-containing compounds decreased and aromatic hydrocarbons increased.

Shown in Fig. 2a are the approximate relative abundances of compounds representing various heteroatomic classes in the coal filtrates. Elemental compositions of the organic compounds belonging to different classes are represented by general chemical formulae. O_xN_y refers to compounds containing C, H, N and O (subscripts x and y provide the number of oxygen and nitrogen atoms per molecule, respectively.). O_x class contains C, H and O, and CH refers to compounds containing only C and H. Sulfur-containing compounds were not identified due to low abundance and/or ionization efficiency. Six major classes were observed for the sample that had not been catalytically treated and five major classes were left after catalytic deoxygenation. The relative abundances of O₂ and O₃ classes decreased from 37% and 15% to 18% and 6%, respectively. Further, an enhanced relative abundance of O₁ class was observed after catalytic deoxygenation. This is likely due to partial deoxygenation of the compounds in other O_x classes (x = 2, 3 or 4), inducing the formation of molecules with a reduced number of oxygen. In general, the total relative abundance of O_x classes decreased because of catalytic deoxygenation and in turn the relative abundance of hydrocarbons (CH) increased. Similar results are also exhibited in the bulk elemental analysis for F1 and F2 as listed in Table S4.

Plots of the double-bond equivalence (DBE) as a function of carbon number for compounds of the O₁ class detected in the coal filtrates are shown in Fig. 3. DBE represents the degree of unsaturation and cyclic structures in the compounds while carbon number correlates loosely with the extent of cracking of the macromolecules in coal [24,25]. Although the relative abundance of O₁ class has increased after catalytic deoxygenation (Fig. 2a), the number of O₁ compounds has decreased by 36% (from 189 to 121) upon deoxygenation (Fig. 3), and the average DBE value and carbon number have decreased after deoxygenation. Aromatic cores connected by alkyl chains are regular molecular structures in coal [26], which are also known as archipelago structures [27]. The removal of molecules with the highest carbon numbers may relate to the cleavage of alkyl chains connecting aromatic cores, suggesting the existence of archipelago structures [28,29]. Compounds in Fig. 3b are generally produced from catalytic deoxygenation of compounds in O₂, O₃ and O₄ classes (Figs. S2, S3 and S4, respectively), and some of them are the left compounds of O₁ class due to the limit of catalytic efficiency. The weighted mean DBE values for

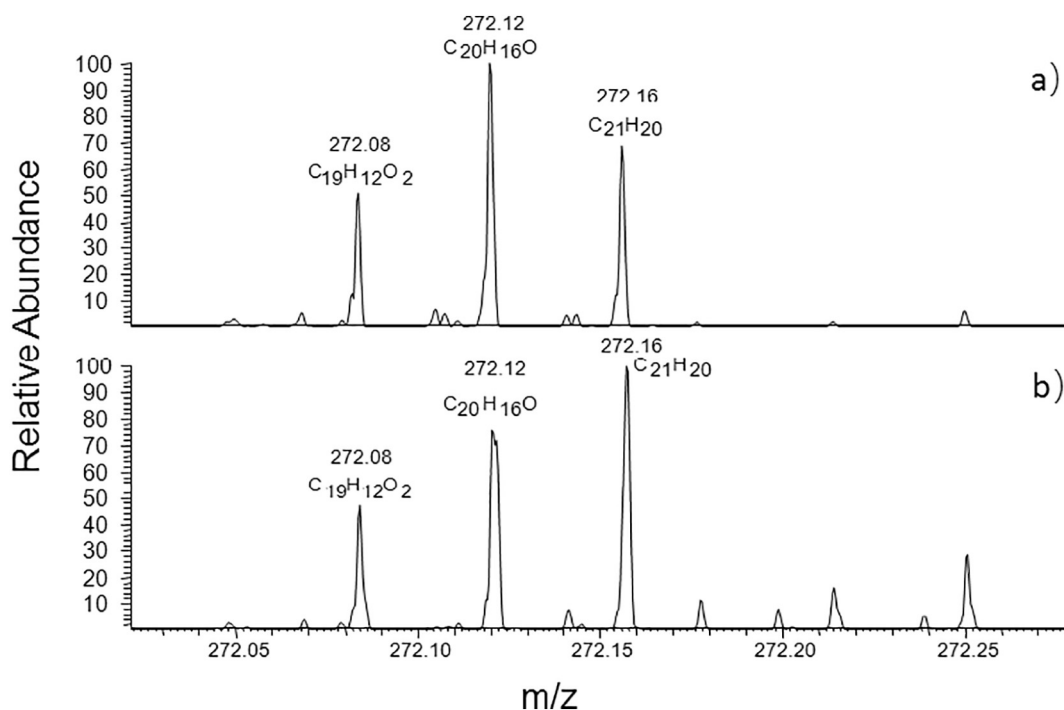


Fig. 1. Mass scale-expanded segments for soluble fractions a) without and b) with catalytic treatment.

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