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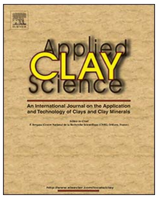

Research paper

Pyrolysis behaviors of organic matter (OM) with the same alkyl main chain but different functional groups in the presence of clay minerals

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ABSTRACT

Organic matter (OM)-clay mineral complexes, especially OM-clay interlayer complexes, exist widely in soil, sediment, and source rock. These associations can influence the pyrolytic behaviors of OM. In addition, the nature of OM may also affect pyrolysis due to the variety and complexity of the structure and chemical composition of natural organics. In this study, to investigate the influences of the nature of OM as well as the interface association between OM and clay minerals on the pyrolysis of OM, interlayer clay-OM complexes and clay-OM mixtures were prepared and thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR) was adapted to monitor the pyrolytic temperatures and products of these complexes. A series of OM with the same alkyl main chain but different functional groups, i.e., Lauric acid (LA), Dodecylamine (DA), 12-Aminolauric acid (ALA) and Dodecyl trimethyl ammonium bromide (DTAB), was used, and montmorillonite (Mt) was selected as the representative clay mineral. The results showed that Mt decreased the decomposition temperature of the carboxyl groups that contained OM (LA and ALA), promoted the generation of CO_2 via the catalysis of the Lewis acid sites of Mt, and delayed the decomposition of DA and DTAB. The interlayer Brønsted acid sites allowed the nitrogen-containing organics to undergo Hoffmann elimination. The pyrolytic behaviors of OM within the interlayers of Mt were more strongly affected than those on the external surface of Mt The pyrolytic performance of OM was closely related to the association ways between OM and clay minerals, the nature of clay minerals, and the nature of OM. The interlayer space was shown to be particularly important for the preservation and catalysis of organics.

1. Introduction

The catalytic functions of clay minerals for natural hydrocarbon generation have been well demonstrated in numerous studies (Jurg and Eisma, 1964; Shimoyama and Johns, 1971; Heller-Kallai et al., 1984). The clay minerals of the smectite group, such as montmorillonite (Mt), have received particular attention because of their known catalytic activities and their ubiquity in low-maturity source rocks and sediments. Traditionally, model organic matter (OM), such as kerogen and bitumen that were separated from source rocks, and synthetic organics, such as fatty acids and fatty acid esters, were mixed with clay minerals, and these mixtures were used in pyrolysis experiments to explore the pyrolytic behaviors of organics in the presence of clay minerals (Jurg and Eisma, 1964; Shimoyama and Johns, 1971; Faure et al., 2003; Li et al., 2003; Zhang et al., 2005; Faure et al., 2006). Under this scenario, OM and clay were assumed to exist separately and the catalytic effects of clay minerals were believed to occur merely on the external surface of clay minerals.

However, in the past several decades, this knowledge has been revised based on the findings of the wide existence of clay-OM associations in sedimentary rocks, which have been demonstrated by a variety of independent studies (Bergamaschi et al., 1997; Ransom et al., 1998; Mayer, 1999; Ingalls et al., 2004; Mayer, 2004; Lopez-Sangil and Rovira, 2013; Zhu et al., 2016). These mentioned studies have verified that in many cases, OM in sediments is primarily associated with clay minerals rather than existing alone. This is indicated by observations that it is difficult to separate organic material from clay minerals using physical methods, as well as the direct proportionality between the concentration of organic matter and the sediment surface area (Keil et al., 1994; Mayer, 1994).

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Particularly, a special clay-OM association in natural sedimentary environments, i.e., the storage of OM within the interlayer space of layered silicates, has been proposed as early as the 1970s (Theng, 1974) and confirmed by a series of following studies (Perezrodriguez et al., 1977; Theng et al., 1986; Kennedy et al., 2002; Cai et al., 2007). From the perspective of surface chemistry properties of swelling clay minerals, there are a variety of natural polar or charged organics, including ammonium ions, that are chemically similar to the model organics used in this study (He et al., 2005; Xi et al., 2007; Zhu et al., 2009), humic acid (Wang and Huang, 1986), and proteins (Yu et al., 2013), which could be intercalated into the interlayer of swelling clay minerals through cation-exchange reactions. Particularly, once the interlayer space is opened through the intercalation of the abovementioned organics, more types of organics, including neutral or nonpolar molecules that initially cannot enter pristine interlayer sites through cation-exchange, could also be intercalated into interlayer space through interactions, such as hydrophobic interactions with preintercalated organics (Lagaly et al., 2013).

The existence of naturally occurring interlayer clay-OM complexes has been demonstrated in a variety of studies in which the interlayer distance of Mt or mixed-layered Mt-illite in source rocks or sediments was found to be expanded due to the intercalation of natural organics (Perezrodriguez et al., 1977; Theng et al., 1986; Schulten et al., 1996; Lu et al., 1999; Kennedy et al., 2002; Cai et al., 2007; Zhu et al., 2016). Theng et al. (1986) reported the occurrence of interlayer clay-organic complexes in the clay fraction of soil samples from Maungatua, New Zealand; the interlayer organics, as revealed by ^{13}C NMR spectroscopic analyses, comprised polymethylene chains containing carboxyl and hydroxyl groups (Theng et al., 1986). Schulten et al. (1996) characterized the organic matter in the interlayer clay-organic complexes from the Maungatua soil using pyrolysis methylation-mass spectrometry (Schulten et al., 1996). Lu et al. (1999) investigated the OM-clay associations in immature source rocks from the Dongying depression of the Bohai Bay Basin, China, and found that the content of the interlayer organics accounted for approximately 25%–50% (mass%) of the total extracted organics (Lu et al., 1999). Kennedy and Wagner (2011) identified the occurrence of OM-clay complexes in Late Cretaceous black shales from the Ocean Drilling Program site 959 of the Deep Ivorian Basin, where OM was located within the interlayer sites of the mixed layer illite-smectite (Kennedy and Wagner, 2011). Recently, Kennedy et al. (2014) further obtained direct high-resolution transmission electron microscopy (HRTEM) evidences of occurrence of OM as nanometer-scale intercalations in swelling clays.

Given the understandings of the OM-clay associations revealed by the abovementioned studies, it is obvious that the roles of clay minerals, especially the swelling clay minerals whose interlayers are able to host OM, in the pyrolysis of OM must be reevaluated. Meanwhile, natural organics with various structures and chemical compositions exhibited different evolutions. For example, three main types of kerogen were identified, from I, starting at low maturity with high H/C and low O/C, to III, starting at low maturity with low H/C and high O/C. It was widely accepted that the type of kerogen largely influenced both the amount and chemical composition of the products generated upon burial (Vandenbroucke and Largeau, 2007). Thus, the nature of OM deserves extra attention in assessing their pyrolytic behaviors in the presence of clay minerals.

In this work, a series of OM-clay complexes were prepared for their use in the pyrolysis experiments of OM. Montmorillonite (Mt) was used as a model clay mineral because of its ubiquity in the source rock and its high expanding capacity. Lauric acid ($CH_3(CH_2)_{10}COOH$, hereafter denoted as LA), Dodecyl amine ($CH_3(CH_2)_{11}NH_2$, DA), 12-Aminolauric acid ($NH_2(CH_2)_{11}COOH$, ALA), and Dodecyl trimethyl ammonium bromide($CH_3(CH_2)_{10}CH_2N(CH_3)_3Br$, DTAB) were selected to represent the natural OM. The selection of the model organics was mainly based on two considerations: the nature of the organics and different mechanisms of OM-clay associations, namely, both interlayer OM-clay complexes synthesized by cation-exchanging (Xi et al., 2007) and OM-clay complexes made by traditional simple mixing (Tannenbaum et al., 1986) were used. These aliphatic organics have similar structures and compounds as some important precursors of oil and gas, such as fatty acids, amino acid, and alkane (Jurg and Eisma, 1964; Liu et al., 1997). In addition, they contain equal lengths of straight-carbon chains but different representative functional groups, which is desirable for the purpose of comparing the pyrolysis mechanisms of these organics. Furthermore, based on the knowledge of intercalation chemistry of clay minerals (Lagaly et al., 2013), both DTAB and DA can be readily cationized and thus can be intercalated into the interlayer of Mt via cation exchange to prepare interlayer clay-OM complexes; ALA is also easily transformed to a protonated amino group ($-NH_3{}^+$) in acidic solution (Liu et al., 2013); in contrast, intercalation of LA into Mt cannot occur because LA is non-ionic, which allows to compare the interlayer associations and the associations occurring at external surface of Mt.

Thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR) was used to investigate the pyrolytic behaviors of OM, which is an effective on-line technique to continuously monitor the mass loss of samples during heating and to simultaneously capture compositional information about the corresponding gaseous products in order to highly efficiently detect the mechanisms of pyrolysis.

2. Experiments

2.1. Materials

LA and ALA were supplied by Tokyo Chemical Industry Co., Ltd., DTAB and DA was purchased from Sigma-Aldrich, Co. LLC. These chemical reagents were used without further purification. The raw montmorillonite with the purity of 97% was obtained from Inner Mongolia, China. Before contacted with OM, montmorillonite was sodium modified to get a better swelling property (hereafter labeled as Mt). The chemical compositions (wt%) of Mt are as follows: SiO_2 56.24%, Al_2O_3 14.96%, Fe_2O_3 4.23%, CaO 0.35%, MgO 4.11%, Na_2O 3.13%, K_2O 0.14%, MnO 0.02%, TiO_2 0.31%, P_2O_5 0.03%, and the ignition loss 16.49%. The cationic exchange capacity (CEC) of Mt is 110.50 mmol/100 g.

Two preparation methods, for the complexes where OM exists at the external surface of Mt and for the interlayer complexes, were used. For the former complex, a total of 10 g of Mt sample and 2.5 g of OM were simply mixed and the mixture was ground by ball milling for 20 min using a Pulverisette-6 Planetary Mill. These products were denoted as LA-Mt, DA-Mt, DTAB-Mt, and ALA-Mt, corresponding to the used organics, respectively. The preparation of interlayer OM-Mt complex was performed according to the following procedure. At first, 22.1 mmol ALA were added into 200 mL of 0.14 M HCl solution and kept at 80 °C water bath; then the resultant solution was added into the dispersion composing of 10 g Mt and 1000 mL distilled water to form a mixture; after stirring at 80 °C for 30 min, the solid in the mixture was filtered and repeatedly washed (8 times) with large amounts of hot distilled water, then freeze-dried and ground to powder. The product was labeled as ALA_{inter}-Mt. The preparation of DA_{inter}-Mt and $DTAB_{inter}$-Mt was similar to the above procedure, except the omission of protonation. LA was not used to prepare interlayer OM-Mt complex because it could not be intercalated into the interlayer space of Mt through cation-exchange. All of the above final products were passed through 200 mesh screen for further use except DA-Mt (Because DA melts after grounding, DA-Mt is easy to bind).

2.2. Instruments and methods

The X-ray diffraction (XRD) patterns of samples were recorded on a Bruker D8 Advance diffractometer with Ni filter and CuKα radiation ($\lambda = 0.154$ nm) using a generator voltage of 40 kV and a generator current of 40 mA, with a scan rate of 3° (2θ)/min.