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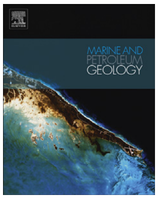

Research paper

Influence of minerals and iron on natural gases generation during pyrolysis of type-III kerogen

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ABSTRACT

Pyrolysis experiments in a closed system were conducted on kerogen (isolated from a low mature coal sample) either in the presence or absence of clay minerals, iron-bearing minerals, transition metal and their mixture, respectively. The generated gases were collected and analyzed for chemical compositions by using gas chromatography and mass spectrometer; the solid residues were also quantitatively collected and analyzed for iron species using Mössbauer spectroscopy. These experiments revealed that the hydrocarbon gases generation from kerogen was significantly increased by catalysis of minerals and transition metal (iron). The generation of hydrocarbon gases could be potentially increased by 0.1–1.5 times in the presence of minerals and iron, and the catalytic efficiency was in the order of kerogen + mixed catalysts > kerogen + pyrite > kerogen + smectite > kerogen + iron > kerogen. The dryness ratios, including ethene/ethane, propene/propane, isobutane/*n*-butane and isopentane/*n*-pentane, were all decreased due to the catalysis of smectite, pyrite and mixed catalysts, and slightly increased with iron addition. The conversion of pyrite into pyrrhotite and elemental sulfur started at 300 °C during the experiments, for which pyrite might be as an inducer indirectly via sulfur and thus enhance the free radical formation and improve the hydrocarbon yield.

1. Introduction

Numerous studies have been established that the transition metals and mineral matrixes are important factors to control the processes of hydrocarbon gases generation, and even influence the resources evolution of crude oils and natural gases (Hunt, 1987; Huizinga et al., 1987). Conventionally, two types of geological catalysts have been mainly considered in terms of active effects on hydrocarbon gases generation, which are natural minerals and elements (Tissot et al., 1974; Johns, 1979; Mango, 1996; Vassileva and Vassilev, 2006). The minerals mentioned for such effectivity include clay minerals (i.e. kaolinite, smectite and illite), iron-bearing minerals (pyrite and siderite), carbonate minerals (like calcite and dolomite) and others (Espitalie et al., 1980; Li et al., 1998; Chen et al., 2000; Pan et al., 2008); and the elements mainly include transition metals (i.e. Fe, Co and Ni) and elemental sulfur and/or other species of sulfur (Attar, 1978; Mango and Hightower, 1997; Lewan, 1998; Medina et al., 2000). Kerogen with smectite or kaolinite maybe typically able to stimulate the conversion of previously generated hydrocarbon gases into low-molecular-weight hydrocarbons (C_7–C_{12}), being probably due to Lewis acidic activity caused by smectite and kaolinite (Johns, 1979; Pan et al., 2010). The role of pyrite in kerogen pyrolysis has been discussed in few studies and reached the following agreements: (1) the decomposition of pyrite in coals could be decreased at 100 °C than that without hydrocarbons, suggesting the indigenous hydrocarbons with hydrogen donor as a key factor to determine the transformation of pyritic sulfur into organic sulfur (Chen et al., 2000); (2) pyrite might directly influence the evolution of wet shale gases (C_2–C_5) and also the hydrocarbon gases generation associated with H_2S through low valence sulfur species such as S^0, and pyrite might also lead to the reversal of stable carbon isotope at temperatures exceeding 504 °C (Wang et al., 2014); and (3) pyrite, whether endogenous or exogenous, could enhance coal conversion and improve hydrocarbon gases yield under hydro-liquefaction

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conditions (Baldwin and Vinciguerra, 1983). In addition, calcite and dolomite are positively effective for the α-olefines generation, but negatively effective for methane generation (Pan et al., 2008). Transition metals such as Ni in source rocks have been advocated as catalysts in determining extent, composition, and timing of natural gases generation (Mango, 1996). However, some recent studies revealed that the transition metals could enhance gases generation and oil cracking, but had no effect on methane yield or enrichment (Lewan et al., 2008). Sulfur, a unique active element, is significant for hydrocarbons generation and also considered as a key factor for low matured crude oils formation (Lewan, 1998).

However, the catalytic role of minerals/elements for hydrocarbon gases generation is still unclear. Different viewpoints, experimental designs and methods may lead to different opinions about the catalytic action of the same substances. The existence of clay minerals may play a significant role in the formation of isomeric hydrocarbons, but may not do so for the natural gases dominated by n-alkanes. Such a disagreement may suggest that the effect of free radicals on hydrocarbon gases generation should be important, but received less attention (L.M. Wu et al., 2012). In comparison with clay minerals, the catalytic effect of iron-bearing minerals has been limitedly studied and the action mechanism is still unclear (Bakr et al., 1991; Larsen and Hu, 2006).

There is always more than one geological catalyst together with organic matters in natural source rocks. By considering various kinds of minerals and metal elements enriched and co-existed in coal, it should be emphasized that a mixed or complex catalytic effect of these minerals/metal elements may contribute to hydrocarbon gases generation. Based on an investigation of coal stratum in China, smectite, pyrite and iron are the three major minerals/transition metal catalysts in coal with contents of 10–30%, 2–15%, and 0.2–0.4%, respectively (Li, 1992; Tomkins, 2010; Y.Y. Wu et al., 2012; Ma et al., 2015). According to the mineral and elemental concentrations in the source rocks mentioned above, a mixed catalyst set was prepared for the pyrolysis experiments, (smectite 30%) + (FeS_2 10%) + (Fe 0.5%) with kerogen, to reveal the effect of minerals/transitional metal on natural gases generation and explain their mechanisms.

2. Experimental

2.1. Samples

The kerogen (Ker) used in this study was obtained from a brown coal ($Ro = 0.47\%$) from the eastern Junggar Basin, NW China, whose geochemical properties were summarized in Table 1. The basic geochemical parameters suggested that it was a low-matured sample dominated by humic matters (type III) and suitable for the study on hydrocarbon gases generation by pyrolysis experiment. Soxhlet extraction of the coal was performed for 72 h by using trichloromethane to remove the original soluble bitumen. The bitumen-free powder sample (approximately 200 meshes) was treated with HCl and HF to remove the carbonate and silicate minerals present in the sample by using the methods described in detail in the literature (Pan et al., 2008). Clay minerals and iron-bearing minerals were not detected in the prepared kerogen by X-Ray powder Diffraction (XRD, data not shown here). The organic carbon content of the prepared kerogen was 85.6%, as measured by using a Rock-Eval instrument, which confirmed the kerogen used as typical type-III accordingly. The pyrite and smectite used in this study were purchased from National Research Center for Certified Reference Material (NRCCRMS) of China. The purity of the pyrite was more than 95%. Chemically pure iron (powder or brocks) was produced by Tianjin Chemical Reagent Co., Ltd.

2.2. Pyrolysis experiments

Due to shortage of suitable commercial tools, the homemade glass tubes were used for all the experiments, whose size is approximately 2 cm of outside diameter, 1.8 cm of inside diameter and 23 cm in length. Five groups (sets) of pyrolysis experiments were performed for different test samples, including group A, the kerogen only (about 200–950 mg); group B, kerogen and smectite (about 200–950 mg kerogen and 30 wt.% smectite); group C, kerogen and pyrite (about 200–950 mg kerogen and 10 wt.% pyrite); group D, kerogen and iron (about 200–950 mg kerogen and 0.5 wt.% iron); group E, kerogen and compositional catalysts (about 200–950 mg kerogen + 30 wt.% smectite + 10 wt.% pyrite + 0.5 wt.% iron). After the test samples loaded, the open end of each tube was purged with argon before being squeezed in a water stopper to create an initial seal, which was subsequently welded in the presence of argon. During welding, the previously welded end was submerged in cold water to prevent reactant heating and then the tubes with samples were heated to a desired temperature for 3 h (initial heating) followed by isothermally heating for 72 h. The temperature control was within ±1 °C. After the pyrolysis experiment, gases were qualitatively collected by using a proper displacement method.

2.3. Gas composition measurement

All gas samples were analyzed for chemical and isotopic composition at Key Laboratory of Petroleum Resources Research, Chinese Academy of Sciences (Lanzhou, China). The composition of major gases were determined by using both static mass spectrometer (model MAT271) and gas chromatography (model GC5890A), with errors below 5% based on repeated measurements of in-house standards, and with a main gas limit of 1 ppm.

2.4. Mössbauer spectroscopy

The Mössbauer spectra were measured at 293 K using a MA-260 (Bench MB-500) Mössbauer spectrometer with a γ-ray source of 0.925 GBq, $^{57}Co/Rh$. The measurement and curve fitting procedures were described elsewhere (Matsuo et al., 1994). The measured spectra were fitted to Lorentzian line shapes using standard line shape fitting routines. The half-width and peak intensities of the quadruple doublet were constrained to be equal. Isomer shifts were expressed with respect to the centroid of the spectrum of metallic iron foil ($^{56}Fe > 99.85\%$).

3. Results

3.1. Gas composition

The amounts of ΣC_{1-5} were consistently increased from a range

Table 1
Total organic carbon (TOC) and Rock-Eval pyrolysis data from the experimental samples.

Sample No.	Depth (m)	Stratum	TOC (%)	S_1-peak (mg/g rock)	S_2-peak (mg/g rock)	Ro (%)	T*max* (°C)
OS	1846	J_1b	73.8	13.6	177.1	0.47	428

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