



Full Length Article

Gas generation and its isotope composition during coal pyrolysis: The catalytic effect of nickel and magnetite

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ABSTRACT

Pyrolysis experiments were conducted at 370–550 °C for 72 h in closed gold capsules to investigate the effect of nickel and magnetite on gas generation from coal in the absence and presence of water.

Nickel had a great catalytic effect on the yield, molecular and carbon and hydrogen isotope composition of generated gases. The methane yields increased significantly while heavy hydrocarbon gas yields decreased substantially due to the catalysis of nickel both in the absence and presence of water. The nickel catalysis caused an increase of $\delta^{13}\text{C}_{\text{CH}_4}$ value in the absence of water and a decrease of $\delta^{13}\text{C}_{\text{CH}_4}$ value in the presence of water. Results of molecular and carbon isotopic composition of hydrocarbons indicate that nickel could catalyze the decomposition of high-molecular-weight organic matter and Fischer-Tropsch-type (FTT) reactions both of which were responsible for the increased methane yield. FTT reactions catalyzed by transition metals are an important pathway for methane generation, especially in the presence of water. The catalytic decomposition of organic matter and FTT reactions also caused an increase of $\delta^2\text{H}_{\text{CH}_4}$ value both in the presence and absence of water. CO_2 yield and $^{13}\text{C}_{\text{CO}_2}$ value increased obviously in the presence of nickel due to the catalytic decomposition of organic matter.

In experiments without added water, addition of magnetite enhanced CO_2 yield at all temperatures but only enhanced methane yield slightly at high temperature (430–550 °C). The increased CO_2 and methane yields can be attributed to the oxidative decomposition of long-chain hydrocarbons via redox reactions between magnetite and hydrocarbons. In experiments with added water, addition of magnetite only caused a slight increase of methane and CO_2 yields at 500 °C and 550 °C but did not influence their yields at 370–450 °C, indicating that water inhibited the effect of magnetite on methane and CO_2 generation at low temperature. The addition of magnetite did not have systematic influence on carbon and hydrogen isotopes of hydrocarbon gases and carbon isotopes of CO_2 . Generally, the influence of magnetite on gas generation was very small.

1. Introduction

The roles of transition metals and minerals in hydrocarbon generation have been widely investigated with pyrolysis experiments under different conditions [1–8]. The transition metals have been demonstrated to be able to catalyze the decomposition of oil and hydrocarbon compounds and lead to the generation of methane-enriched gases which resemble the natural gas in molecular and isotopic composition [1,2,4,9–11]. However, there are also some arguments against the catalysis of transition metals. For example, a recent experiment revealed that the effect of transition metals under hydrous condition was not as pronounced as that under nonhydrous condition [7]. Also, no catalytic effect was observed in hydrous pyrolysis of Permian

Kupferschiefer which is rich in transition metals [5]. So it is necessary to reevaluate the effect of transition metals on the decomposition of organic matter under different conditions with further experiments. In addition to the catalytic effect on the decomposition of organic matter, transition metals were demonstrated to be good catalysts for Fischer-Tropsch-type (FTT) reactions through which hydrocarbon gases can be synthesized from CO_2 and H_2 [12–17]. Since both CO_2 and H_2 can be generated from decomposition of organic matter [18–20], the FTT reactions may also occur in sedimentary basins in the presence of transition metals and therefore should be carefully considered when discussing the role of transition metals in hydrocarbon gas generation.

The role of iron-bearing minerals in hydrocarbon generation has received less attention compared with transition metals and most

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previous works focused on the effect of pyrite on hydrocarbon generation [6,21]. The role of iron oxides, however, has been rarely discussed. Iron oxides present in sedimentary basins were suggested to be reactive oxidizing agents for hydrocarbons and could influence the composition and yield of pyrolysis products [22,23]. So the effect of iron oxides on hydrocarbon gas generation may be a significant issue which has been neglected in previous studies.

Most pyrolysis experiments employed to evaluate the role of minerals and transition metals focused on the yields and compositions of pyrolysis products, while the isotopic composition of products, which may provide important information, have received less attention [1,3,4,6,9,11,21]. In this study, six series of pyrolysis experiments were conducted on a coal sample in closed gold capsules at 370–550 °C for 72 h and the yields, compositions and stable carbon and hydrogen isotopes of hydrocarbon gases were measured to investigate the role of nickel and magnetite in gas generation from coal in the absence and presence of water.

2. Experiment

2.1. Starting material

The coal used in this study was sampled from the Lower Cretaceous Shahezi Formation in Jilin Province, China. The geochemical properties of the coal are shown in Table 1. The coal was crushed to 120 mesh and dried at 100 °C for 2 h. The distilled water used in the experiments is a H-O isotopic standard substance (GBW(E)070016) developed by Chinese Academy of Geological Sciences. The standard water was obtained through filtration and distillation of seawater and has a $\delta^2\text{H}$ value of -4.8‰. Powdered silicon-aluminum-supported nickel and magnetite (> 200 mesh) were obtained from Alfa Aesar. Nickel content in the silicon-aluminum-supported nickel is 61.4%. The purity of magnetite is 99.997%.

2.2. Pyrolysis experiment

The pyrolysis experiments were conducted in gold capsules (50 mm length \times 5.5 mm o.d.; 0.5 mm wall thickness). One end of the capsule was sealed with argon-arc welding. Then coal or mixture of coal and magnetite or nickel were loaded into capsules. And then, water was injected into capsules with a glass syringe for experiments with added water. After the loading of starting materials, the air in headspace of capsules was expelled by argon before final sealing of capsules with argon-arc welding. The previously welded end of the capsule was submerged in cold water during the final sealing to avoid heating of samples and evaporation of water.

The gold capsules with reactants were heated in steel pressure vessels which were filled with water as the pressure-controlling medium. The internal water pressure of the vessels was adjusted to 40 MPa by pumping water in and out of the vessels with an air-driven pump. The water pressure could be easily transmitted into the gold capsules due to the good elasticity of the gold metal [12]. Therefore, all pyrolysis experiments were carried out under a constant pressure of

Table 1
Geochemical parameters of the coal.

Sample	Ro (%)	TOC (wt. %)	S ₁ (mg HC/g rock)	S ₂ (mg HC/g rock)	S ₃ (mg CO ₂ /g rock)	T _{max} (°C)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)
YC-01	0.62	63.6	0.92	120	3.6	422	187	6

Ro: vitrinite reflectance; TOC: total organic carbon; S₁: free hydrocarbon; S₂: pyrolysis products from cracking of organic matter; S₃: CO₂ released during pyrolysis; T_{max}: the temperature at which the S₂ peak reaches its maximum; HI: hydrogen index (S₂/TOC \times 100); OI: oxygen index (S₃/TOC \times 100) [24].

40 MPa. Each vessel was loaded with 6 gold capsules with different starting materials (coal alone, coal plus water, coal plus nickel, coal plus water and nickel, coal plus magnetite and coal plus water and magnetite) and heated to the designated temperature (370 °C, 400 °C, 430 °C, 450 °C, 500 °C and 550 °C) at a heating rate of 20 °C/min and held at the designated temperatures for 72 h.

2.3. Chemical and isotopic analysis of gas components

A customized device was used to extract and quantify the gaseous products in gold capsules as described previously [12]. Briefly, the device was made up of a glass vessel in which gold capsules were pierced, a vacuum pump and a pressure gauge. The glass vessel was evacuated to an initial pressure (P₁, less than 1×10^{-3} bar) by the vacuum pump after the loading of gold capsules. Then the capsules were pierced and pressure in the glass vessel would increase to P₂. The volumes of gas products can be calculated with the equation: $V = (P_2 - P_1) \times V_0/P_0$ (V₀ is the volume of gas collection unit, P₀ is the atmosphere pressure).

The composition of gas was analyzed with a two-channel Wavon-Agilent Agilent 7890 Gas Chromatograph which was equipped with two capillaries and six packed columns, a flame ionization detector and two thermal conductivity detectors (TCD).

Carbon isotopic composition of hydrocarbons was analyzed on a Thermo Delta V mass spectrometer interfaced with a Thermo Trace GC Ultra gas chromatograph (GC). The stable carbon isotopic value was reported in the δ -notation in per mil (‰) relative to the Vienna Pee Dee Belemnite standard (VPDB). Analytical error was less than $\pm 0.3\%$. Stable hydrogen isotopic composition was analyzed with a GC/TC/IRMS mass spectrometer, which was made up of a Trace GC Ultra gas chromatograph (GC), a micro-pyrolysis furnace (1450 °C) and a Finnigan MAT253 mass spectrometer. The hydrogen isotopic composition was expressed in the δ -notation in per mil (‰) relative to standard mean ocean water (VSMOW) and the precision was estimated to be $\pm 3\%$ [25].

3. Results and discussion

3.1. Effect of nickel on hydrocarbon gas generation

The form of transition metal is an essential issue in the discussion of catalysis. It is controversial about the form of nickel in natural system. Some researchers argued that NiO may be a possible form of nickel present in natural system and it can be reduced by H₂ in the reducing conditions in sedimentary basins [2,4,26]. So reduced nickel oxide (NiO) was typically used in previous catalytic experiments [1,2,4]. As demonstrated by Medina et al. [4], NiO could be reduced to Ni metal during the pretreatment in H₂ in previous works and the Ni metal rather than NiO was proved to be the active catalyst. Therefore, silicon-aluminum-supported nickel metal without any further treatment was used in our experiments.

As shown in Table 2 and Fig. 1, nickel has a great catalytic effect on the yield and composition of hydrocarbon gases. The yields of methane increased by 83–1541% and 150–1350% due to the catalysis of nickel in the absence and presence of added water, respectively (Table 2, Fig. 1a). The heavy hydrocarbon gas yields, however, decreased dramatically at all temperatures in the presence of nickel under both conditions (Table 2, Fig. 1b, c). The increase of methane yields and decrease of heavy hydrocarbon gas yields indicate that heavy hydrocarbon gases were catalytically cracked to methane in the presence of nickel. However, the decomposition of heavy hydrocarbon gases can only account for a small fraction of the total increase of methane yield. So we infer that high-molecular-weight bitumen and kerogen also underwent catalytic decomposition process and made contributions to the methane yield increase in the presence of nickel, since they are less thermally stable than hydrocarbon gases. This is consistent with

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