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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 $\delta^{13}C_{CH4}$ value in the absence of water and a decrease of $\delta^{13}C_{CH4}$ 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 δ^2H_{CH4} value both in the presence and absence of water. CO_2 yield and $^{13}C_{CO2}$ 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 δ^2H 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 × 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 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.

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; S_1: free hydrocarbon; S_2: pyrolysis products from cracking of organic matter; S_3: CO_2 released during pyrolysis; T_{max}: the temperature at which the S_2 peak reaches its maximum; HI: hydrogen index (S_2/TOC × 100); OI: oxygen index (S_3/TOC × 100) [24].

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 (P_1, 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 P_2. The volumes of gas products can be calculated with the equation: $V = (P_2 - P_1) \times V_0/P_0$ (V_0 is the volume of gas collection unit, P_0 is the atmosphere pressure).

The composition of gas was analyzed with a two-channel Wasson-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 Peedee Belemnite standard (VPDB). Analytical error was less than ± 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 micropyrolysis 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 ± 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 H_2 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 H_2 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

Table 2
The yields and stable carbon and hydrogen isotopic compositions of gaseous products.

T (°C)	Series	Coal (mg)	Water (mg)	Magnetite (mg)	Silicon-aluminum-supported nickel (mg)	Absolute Amount (mmol/g of Coal)									Mole ratio	$\delta^{13}C$ (‰, VPDB)				δ^2H (‰, VSMOW)	
						CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	CO_2	H_2	H_2S	$\Sigma C_{1\text{-}5}$	$C_1/\Sigma C_{1\text{-}5}$	CO_2	CH_4	C_2H_6	C_3H_8	CH_4	C_2H_6
370	Coal	149.1				0.460	0.099	0.025	0.004		1.054	0.007	0.001	0.588	0.782	−15.5	−33.1	−24.6	−22.0	−309.3	−250.3
	Coal + H_2O	148.9	30.5			0.516	0.138	0.044	0.008	0.001	1.507	0.009	0.002	0.707	0.730	−16.4	−33.8	−25.1	−22.1	−296.0	−232.5
	Coal + Ni	80			80	5.064	0.008	0.001	0.001		5.898			5.074	0.998	−7.2	−31.2			−161.3	
	Coal + Fe_3O_4	92.3		92.4		0.443	0.117	0.030	0.004	0.001	1.297	0.004		0.596	0.744	−16.7	−33.0	−24.4	−22.7	−315.6	−251.9
	Coal + H_2O + Ni	80.5	16		80	6.833	0.023	0.017	0.015	0.003	8.087			6.892	0.991	−11.3	−35.9			−137.2	
	Coal + H_2O + Fe_3O_4	99.8	22.9	99.8		0.428	0.118	0.037	0.006	0.001	1.405	0.004		0.589	0.726	−16.3	−33.1	−24.3	−22.6	−284.6	−230.4
400	Coal	120.9				1.161	0.189	0.037	0.005		1.313	0.017	0.001	1.391	0.834	−16.8	−30.2	−22.5	−20.5	−300.5	−208.2
	Coal + H_2O	122.4	25.3			1.199	0.227	0.062	0.010	0.001	1.634	0.029	0.002	1.499	0.800	−16.7	−30.2	−22.7	−20.9	−282.4	−204.3
	Coal + Fe_3O_4	94.1		94.1		1.105	0.189	0.034	0.004		1.550	0.013		1.332	0.829	−16.6	−30.1	−21.6	−19.6	−300.9	−215.4
	Coal + H_2O + Fe_3O_4	98.4	20.5	98.3		1.061	0.214	0.057	0.009		1.719	0.017		1.341	0.791	−16.7	−30.2	−22.7	−20.5	−287.3	−198.1
430	Coal	104.5				1.815	0.166	0.013	0.001	0.002	1.466	0.029	0.001	1.996	0.909	−16.5	−28.4	−19.6	−13.7	−278.4	−140.2
	Coal + H_2O	102.4	20			2.068	0.256	0.034	0.003		1.957	0.047	0.003	2.360	0.876	−16.5	−28.1	−20.9	−16.5	−268.2	−131.3
	Coal + Fe_3O_4	97.5		97.6		2.055	0.198	0.015	0.001		1.829	0.011		2.269	0.906	−16.2	−28.0	−18.8	−15.1	−281.9	−137.2
	Coal + H_2O + Fe_3O_4	95	20	95		2.032	0.255	0.035	0.003		2.018	0.033		2.325	0.874	−16.1	−28.0	−20.6	−16.4	−268.4	−156.4
450	Coal	79				2.578	0.126	0.003			1.464	0.034	0.003	2.707	0.952	−15.9	−27.0	−15.7	−6.2	−254.0	−124.4
	Coal + H_2O	79.1	16.7			2.830	0.227	0.013	0.001		1.877	0.067	0.002	3.071	0.922	−17.2	−27.0	−18.1	−9.3	−247.2	−105.4
	Coal + Ni	79.5			79.5	7.179	0.010				7.064	0.003		7.189	0.999	−4.4	−22.7			−156.5	
	Coal + Fe_3O_4	79		78.2		2.902	0.157	0.003			1.838	0.012	0.001	3.062	0.948	−16.1	−26.8	−15.5	−5.8	−257.1	−124.8
	Coal + H_2O + Ni	78.5	16.5		78.4	9.983	0.012				10.061			9.995	0.999	−8.3	−28.9			−112.5	
	Coal + H_2O + Fe_3O_4	80	16.2	80		2.870	0.207	0.009			2.016	0.049		3.086	0.930	−16.2	−26.5	−17.7	−8.2	−246.0	−107.0
500	Coal	60				3.667	0.015				1.690	0.066		3.682	0.996	−15.0	−24.1	−8.9	−14.5	−180.8	−147.9
	Coal + H_2O	62.1	12.7			4.184	0.044				2.218	0.122		4.228	0.990	−15.4	−23.8	−5.7	−12.6	−168.7	−111.0
	Coal + Ni	60			60	7.684	0.004				7.058	0.017		7.687	1.000	−1.9	−20.4			−158.9	
	Coal + Fe_3O_4	58.5		58.1		3.920	0.017				2.097	0.021		3.937	0.996	−15.4	−23.5	−7.7	−13.8	−182.1	−148.8
	Coal + H_2O + Ni	58.5	11.7		59	11.971	0.009				11.923	0.016	0.006	11.980	0.999	−5.8	−26.3			−113.4	
	Coal + H_2O + Fe_3O_4	60.4	12.4	60		4.566	0.029				2.501	0.103		4.595	0.994	−15.4	−23.6	−6.5	−12.0	−158.7	−116.4
550	Coal	49.8				4.475	0.007				2.064	0.135		4.482	0.998	−16.2	−22.4	−14.4	−16.6	−164.1	−147.9
	Coal + H_2O	51.2	10			5.587	0.013				2.873	0.256		5.600	0.998	−16.5	−22.1	−11.9	−13.2	−135.4	−122.6
	Coal + Ni	47.8			47.8	8.170					7.504	0.018		8.170	1.000	−4.7	−18.3			−156.3	
	Coal + Fe_3O_4	50.1		50.7		4.859	0.008				2.430	0.128		4.866	0.998	−15.8	−22.0	−13.9	−16.7	−161.7	−146.5
	Coal + H_2O + Ni	50.3	9.8		50.3	13.962					13.906	0.019		13.962	1.000	−10.9	−24.1			−122.7	
	Coal + H_2O + Fe_3O_4	47.2	10.5	47		6.128	0.010				3.252			6.138	0.998	−17.5	−21.9	−11.7		−129.0	−113.3

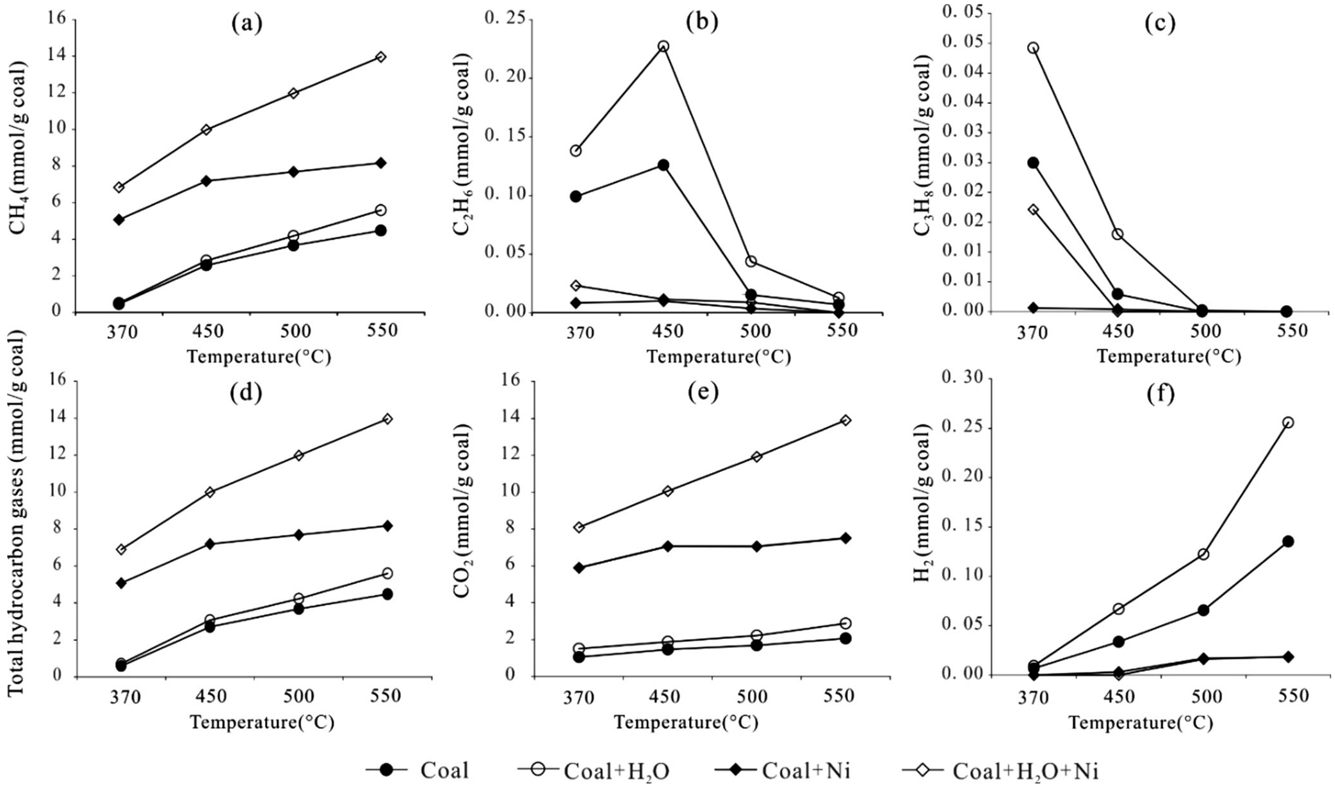

Fig. 1. Selected gas yields produced in experiments using coal, coal + water, coal + Ni and coal + water + Ni.

previous observations that all hydrocarbon types in oil, including *n*-alkanes, isoalkanes, cycloalkanes and aromatics, can be catalytically decomposed to methane in the presence of nickel [1]. The result indicates that the catalytic decomposition of organic matter could occur both in the absence and presence of water.

According to the kinetic isotopic fractionation effects, methane is depleted in ^{13}C compared with higher molecular weight organic precursor, including kerogen, bitumen and heavy hydrocarbon gases. And the catalytic decomposition of higher molecular weight organic compounds will lead to an enrichment in ^{13}C in methane, i.e., an increase of $\delta^{13}C_{CH4}$ value. However, we noticed that $\delta^{13}C_{CH4}$ values in experiments with coal + water + Ni are consistently lower than those in experiments with coal + water (Fig. 2a), which means the nickel catalysis caused a decrease of $\delta^{13}C_{CH4}$ value in the presence of added water. So we can infer that there must exist other pathways responsible for the methane generation in experiments with coal + water + Ni and the methane generated through these pathways should be more depleted in ^{13}C than thermogenic methane in experiments with coal + water.

The Fischer-Tropsch-type (FTT) reactions have been demonstrated to be an important mechanism for hydrocarbon generation in natural system [27]. Fischer-Tropsch-type (FTT) reactions refer to the catalytic reduction of CO_2 or CO in reaction with H_2 to form methane and other alkanes [13,17,28–30]. Much laboratory work has been conducted to evaluate the carbon isotopic fractionation in FTT reactions [12,13,16,17,28,30]. All these published data to date revealed that the generated methane and its homologues were all substantially depleted in ^{13}C relative to the initial carbon source ($\Delta^{13}C$ $_{\text{Initial Carbon-Generated Methane}}$ up to 48.8‰ [16]). Specifically, in experiments with CO_2 as the initial carbon source, $\delta^{13}C$ values of methane generated from FTT reactions were 15.4‰ to 35.0‰ lighter than $\delta^{13}C$ values of initial CO_2 [12,13,30]. Although we do not know the exact $\delta^{13}C$ values of initial CO_2 in experiments with coal + water + Ni, if FTT reactions do occur, it can be inferred that $\delta^{13}C$ values of initial CO_2 should be lighter than those of residual CO_2 (CO_2 yielded in the experiments) due to the carbon isotope balance. The residual CO_2 (CO_2 yielded in the experiments) has $\delta^{13}C$ values of −11.3‰ to −5.8‰ at different temperatures in experiments with coal + water + Ni. So the initial CO_2 should have $\delta^{13}C$ values lighter than −11.3‰ to −5.8‰. The methane generated from CO_2 with such $\delta^{13}C$ values via FTT reactions can be more depleted in ^{13}C than methane in experiments with coal + water ($\delta^{13}C_{CH4} = -33.8‰ \sim -22.1‰$). So the FTT reactions were possible pathways to cause the decrease of $\delta^{13}C_{CH4}$ value in experiments with coal + water + Ni.

Transition metals have been demonstrated to be good catalysts for the FTT reactions. Large amounts of CO_2 were yielded in our experiments (Table 2, Fig. 1e). H_2 was also generated during the coal pyrolysis, especially in experiments with added water (Table 2, Fig. 1f). It is noteworthy that the small H_2 yields in experiments with coal alone and coal + water do not necessarily indicate only small amounts of H_2 were generated during pyrolysis process. It is likely that most generated H_2 was consumed during the hydrocarbon generation from thermal cracking of organic matter. The generated H_2 could participate in FTT reactions in the presence of appropriate catalysts during the pyrolysis process. So the reactants (CO_2 and H_2) and required catalyst (Ni) for FTT reactions were all present in experiments with coal + water + Ni. It has been demonstrated that methane can be generated at high rate via FTT reactions in the presence of nickel [4]. Therefore, the methane generation through FTT reactions is the most likely reason for the decreased $\delta^{13}C_{CH4}$ value in experiments with coal + water + Ni. So we can infer that FTT reactions play an important role in the catalytic methane generation in the presence of water. Thus the increased methane yield in experiments with coal + water + Ni can be attributed to methane generation from catalytic decomposition of organic matter and FTT reactions.

Although the $\delta^{13}C$ values of methane in experiments with coal + Ni were consistently higher than those in experiments with coal alone (Fig. 2a) and therefore did not show compelling evidence for generation of ^{13}C-depleted methane, we still infer that FTT reactions also occurred in experiments with coal + Ni, since CO_2 and H_2 can be also generated in coal pyrolysis without water. The reason for the fact that $\delta^{13}C_{CH4}$

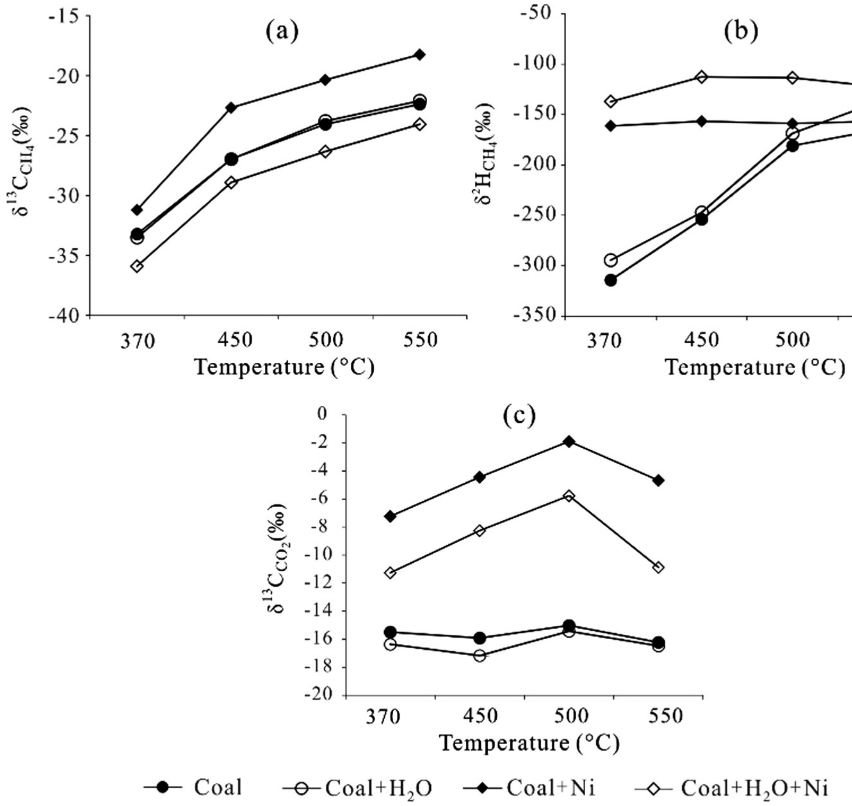

Fig. 2. Isotopic compositions of gases in experiments with coal, coal + water, coal + Ni and coal + water + Ni at 370 °C, 450 °C, 500 °C and 550 °C. (a) Carbon isotopes of methane (b) Hydrogen isotopes of methane. (c) Carbon isotopes of CO_2.

values in experiments with coal + Ni were still higher than those in experiments with coal alone was that shift of $\delta^{13}C_{CH4}$ value towards negative direction caused by the ^{13}C-depleted methane generated via FTT reactions was much smaller than that towards positive direction caused by the ^{13}C-enriched methane generated from decomposition of organic matter in experiments with coal + Ni. So it can be inferred that the catalytic decomposition of organic matter was the dominant catalytic reaction while FTT reactions only played a secondary role in methane generation in the absence of water.

Thus it is most likely that the increased methane yields in experiments with coal + Ni can be also attributed to the methane generation from catalytic decomposition of organic matter and FTT reactions, but the amount of methane synthesized via FTT reactions was much smaller than that in experiments with coal + water + Ni due to the small amount of H_2 generated in the absence of water. Actually, the total methane yields in experiments conducted using coal + water + Ni were systematically higher than those in experiments conducted without water (Fig. 1a). The yield difference of methane generated through FTT reactions should be partially responsible for the total methane yield difference.

The catalytic decomposition of organic matter and FTT reactions in the presence of nickel also led to change of hydrogen isotopic composition of methane. $\delta^{2}H_{CH4}$ values from experiments using coal + Ni and coal + water + Ni were higher than those from experiments conducted without Ni, especially at low temperatures (Fig. 2b). According to the kinetic isotopic fractionation effects, hydrogen in thermogenic methane is more depleted in ^{2}H than hydrogen in heavier molecular weight precursor (including kerogen, bitumen and heavy hydrocarbon gases). The ^{2}H-enriched hydrogen in these heavier molecular weight organic matter could get into methane during the catalytic decomposition process and FTT reactions and therefore caused the $\delta^{2}H$ values of catalytic methane generated in the presence of nickel to be higher than those of methane generated in the absence of nickel. It is noteworthy that $\delta^{2}H_{CH4}$ values from experiments using coal + water + Ni were consistently higher than those from experiments without water (Fig. 2b). The most likely reason for the difference is that water-derived hydrogen, which is rich in ^{2}H ($\delta^{2}H_{H2O} = -4.8‰$), was incorporated into methane during the catalytic decomposition and FTT reactions in experiments using coal + water + Ni.

To sum up, nickel could catalyze the decomposition of organic matter and FTT reactions. The catalysis could lead to a substantial increase of methane yield and hydrocarbon gas dryness. The addition of water facilitated the catalytic methane generation, which was most likely due to the contribution of water-derived hydrogen during catalytic decomposition of organic matter and FTT reactions.

The yields of CO_2 were also enhanced by nickel both in the presence and absence of water (Fig. 1e). In addition, $^{13}C_{CO2}$ value increased obviously due to the catalysis of nickel both in the absence and presence of water (Fig. 2c). The increase of CO_2 yield and $^{13}C_{CO2}$ value in experiments with nickel added can be also attributed to the catalytic decomposition of organic matter.

When discussing the role of transition metals in natural gas generation, the catalytic decomposition of organic matter is a traditional aspect, which has been widely investigated by Mango and co-workers, the CO_2 reduction or hydrogenation via FTT reactions, however, has been addressed in a few studies [4,15]. Medina et al. [4] found that CO_2 can be reduced to CH_4 in H_2 atmosphere in the presence of Ni or Fe and therefore suggested the CO_2 hydrogenation catalyzed by Ni or Fe was an important mechanism for coal-bed gas generation. However, no evidence of transition metal-catalyzed CO_2 reduction (FTT reactions) has been found in the pyrolysis of organic matter without added H_2. This is because previous works only focused on the yield and composition of catalytic hydrocarbon gases which cannot help to distinguish the pathway of methane generation. Our study on both yield and isotopic composition of catalytic hydrocarbon gases demonstrates for the first time that methane can be generated through FTT reactions in the

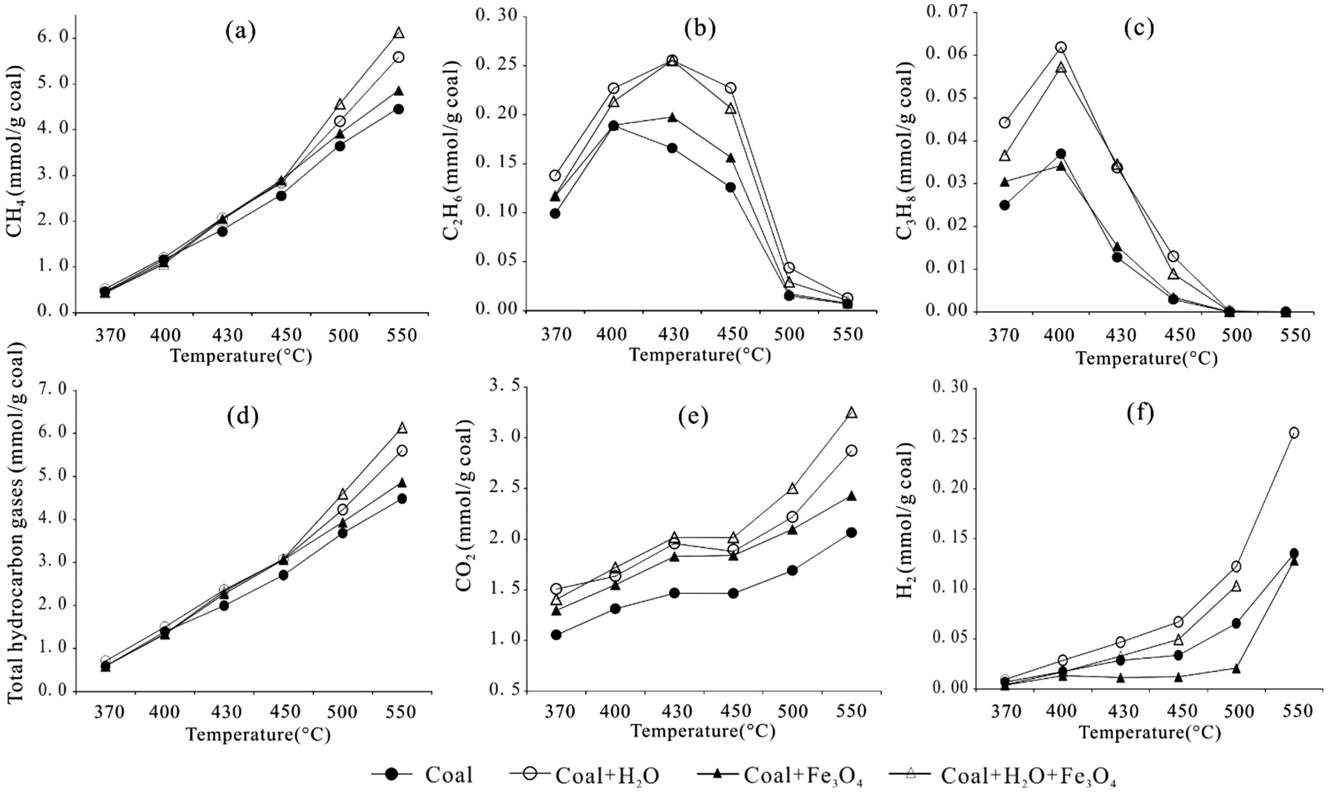

Fig. 3. Gas yields in experiments with coal, coal + water, coal + Fe_3O_4 and coal + water + Fe_3O_4.

presence of transition metal in pyrolysis of organic matter without extraneous H_2.

It can be inferred from our experiments that water plays a significant role in Ni-catalyzed methane generation and the water-derived H can be incorporated into catalytic methane. However, Xia et al. [31] recently demonstrated that water-derived H is unlikely to get into methane in natural system. This conflict may indicate that the Ni-catalyzed FTT reactions and catalytic decomposition process may only occur in some specific circumstances, e.g. places with high abundance of transition metals and high temperature (> 200 °C, which is favorable for FTT reactions).

3.2. Effect of magnetite on hydrocarbon gas generation

Magnetite only had a slight effect on the yields and composition of hydrocarbon gases. As shown in Table 2 and Fig. 3a, the methane yields at 370 °C and 400 °C in experiments with coal + Fe_3O_4 were similar to those in experiments with coal alone (Table 2, Fig. 3a), indicating that magnetite had no effect on methane generation at 370 °C and 400 °C in the absence of added water. However, the yields of methane at higher temperatures (430 °C, 450 °C, 500 °C and 550 °C) in experiments with coal + Fe_3O_4 were consistently higher than those in experiments with coal alone (Table 2, Fig. 3a), which indicated that addition of magnetite enhanced methane generation at high temperatures (430–550 °C).

In contrast to methane, CO_2 generation was enhanced by added magnetite at all temperatures from 370 °C to 550 °C in the absence of added water (Table 2, Fig. 3e). It has been demonstrated that hydrocarbons can be oxidized by ferric-iron-bearing minerals through redox reactions to form intermediate oxygenated compounds which could be decomposed to CO_2 and lighter hydrocarbons [22,23,32,33]. The oxidation of long-chain hydrocarbons can ultimately lead to the generation of CO_2, methane and short-chain hydrocarbons [22,23,32]. CO_2 is the typical oxidative product and its yield is most susceptible to the oxidative process. In addition, methane, as one of the final products in the oxidative decomposition of hydrocarbons, was relatively unreactive in redox reactions and its abundance is also easily influenced by the oxidation process [22,32]. So the enhanced CO_2 yields at all temperatures and increased methane yields at high temperatures (430–550 °C) in experiments with coal + Fe_3O_4 were probably derived from the generation of CO_2 and methane from oxidative decomposition of high-molecular hydrocarbons.

A possible interpretation for the lack of difference on methane yield at 370 °C and 400 °C between experiments with coal + Fe_3O_4 and coal alone is that methane had not been generated from the oxidation of heavier hydrocarbons yet in experiments with coal + Fe_3O_4 at 370 °C and 400 °C. The oxidative decomposition of hydrocarbons consists of a series of reactions. Oxygenated compounds, such as organic acids, alcohols and ketones, were first generated as intermediate products and then transformed to CO_2, methane and other low molecular hydrocarbons [22,32]. It is likely that although the oxidative reactions of hydrocarbons had begun to occur at 370 °C and 400 °C in experiments with coal + Fe_3O_4, which can be indicated by the increased CO_2 yields, the generation of methane, which occurred at higher temperatures, had not occurred at such temperatures (370 °C and 400 °C). Pan et al. [22] also found that the oxidation of heavy hydrocarbon gases occurred at 350 °C within 72 h (with CO_2 yields increased) but methane was only generated from the oxidative process after 72 h, indicating that the generation of methane did occur at a later stage in oxidative process and need more time or higher temperature than the generation of CO_2 during hydrocarbon oxidation process.

Actually, oxidation of hydrocarbons in the presence of redox-reactive minerals (such as anhydrite, magnetite, pyrite and hematite) is a significant process in sedimentary basins [23]. Thermochemical sulfate reduction (TSR) occurring in the presence of sulfate has been accepted as the most prevalent case of oxidative decomposition of hydrocarbons since it can be easily identified in natural system by the increased hydrogen sulfide abundance. The oxidation of hydrocarbons involving iron-bearing minerals, however, has not received much attention because of the lack of distinct evidence for it. But the laboratory experiments have provided compelling evidence for the oxidative

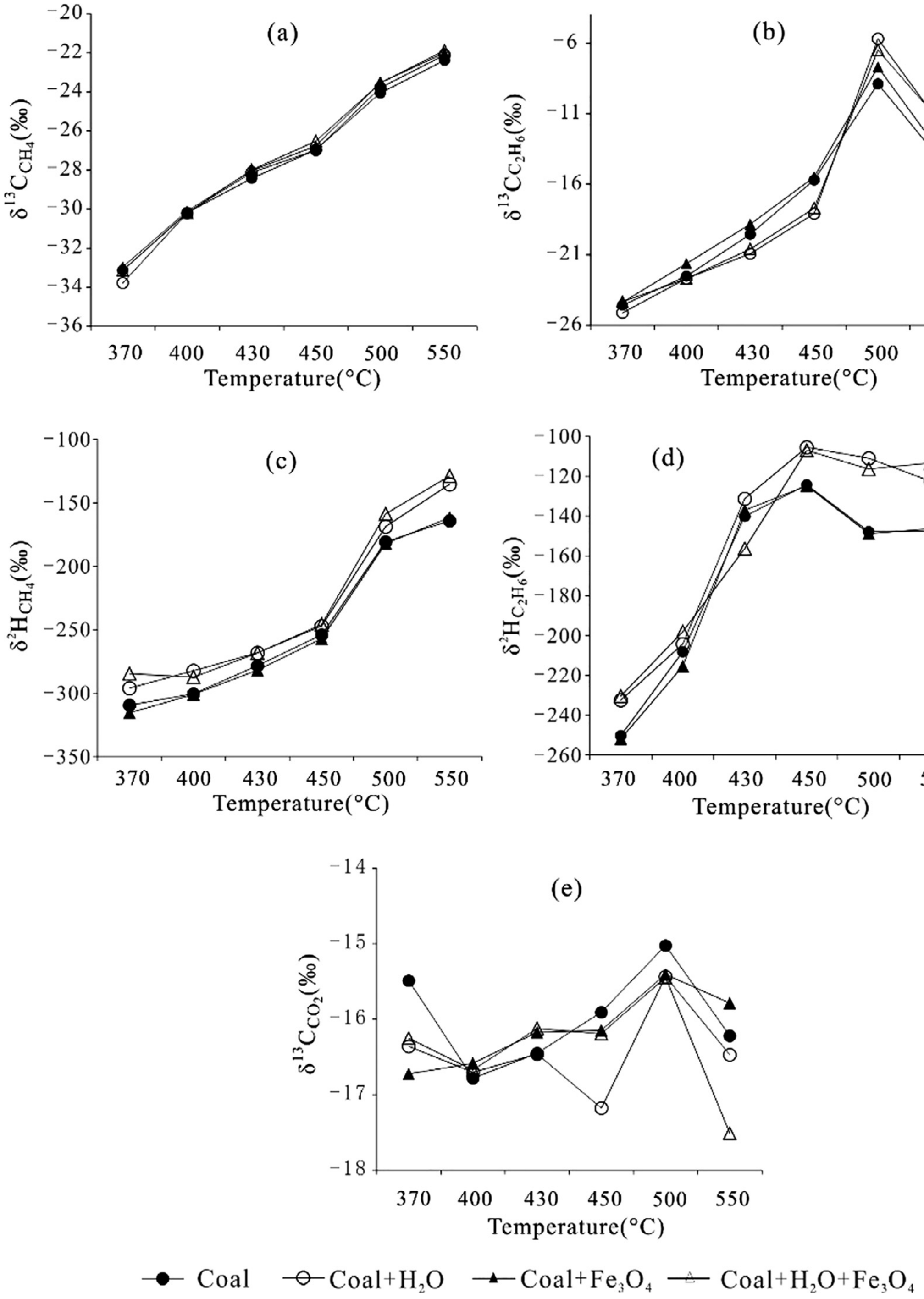

Fig. 4. Carbon and hydrogen isotopes of hydrocarbon gases in experiments with coal, coal + water, coal + Fe_3O_4 and coal + water + Fe_3O_4.

decomposition of hydrocarbons by iron-bearing minerals [22].

Analyzing the experiments with added water, it should be noted that addition of magnetite did not influence the methane yield at 370–450 °C but enhanced methane generation at 500 °C and 550 °C (Table 2, Fig. 3a). Similarly, CO_2 yields were only enhanced by magnetite at 500 °C and 550 °C (Fig. 3e). The lack of variation on methane and CO_2 yields between experiments with and without magnetite at 370–450 °C in the presence of added water indicated that water inhibited the effect of magnetite on CO_2 and methane generation at low temperature. The most likely mechanism for the inhibition was that water suppressed the redox reactions between magnetite and hydrocarbons at low temperatures (370–450 °C).

In addition to the oxidation of hydrocarbons by magnetite, the FTT reactions were also a potential mechanism for the increased methane yields in the presence magnetite since the magnetite has been demonstrated to be able to catalyze the FTT reactions [17,30,34]. However, the FTT reactions cannot interpret the lack of variation of methane yields between experiments with coal + Fe_3O_4 and coal alone at 370 °C and 400 °C. As illustrated by previous abiogenic synthesis experiments, The FTT reactions catalyzed by magnetite were favorable at relatively low temperature (230–400 °C) [17,30,34]. So if FTT reactions had occurred in experiments with coal + Fe_3O_4 at 430–550 °C, they should also occur at 370 °C and 400 °C and cause the increase of methane yields, which is conflict with our result. In addition, as we discussed in

Section 3.1, the addition of small amounts of water could facilitate the FTT reactions in pyrolysis experiments because the H_2 generation can be enhanced in the presence of water. However, in our experiments, the added water inhibited the increase of methane yields at 430 °C and 450 °C. So we infer that the increased methane yields in the presence of magnetite were not derived from methane generation via FTT reactions.

Although the addition of magnetite also caused slight changes of heavy hydrocarbon gas yields, the absolute yield differences of heavy hydrocarbon gases between experiments with and without magnetite were small and seemed somewhat random (Table 2, Fig. 3b, c). In general, magnetite did not have obvious and systematic influence on heavy hydrocarbon gas generation.

Generally, the effect of magnetite on hydrocarbon gas yields was small (Fig. 3a, b, c, d). In addition, the addition of magnetite did not cause obvious change of carbon and hydrogen isotopic compositions of hydrocarbon gases both in the presence and absence of water (Fig. 4). It is likely that the low extent of hydrocarbon oxidation by magnetite and the small amount of oxidative products were not enough to cause an obvious shift of carbon and hydrogen isotopes of hydrocarbon gases. Similarly, addition of magnetite did not lead to systematic change of carbon isotopic composition of CO_2 although there exist some random variations of $^{13}C_{CO2}$ at different temperatures.

It is noteworthy that carbon and hydrogen isotope rollover, which means $\delta^{13}C$ and $\delta^{2}H$ values of specific compounds (e.g. ethane or propane) initially increase with increasing maturity but later display a reversal in trend and decrease with increasing maturity, were observed for ethane in experiments with coal, coal + water, coal + Fe_3O_4 and coal + water + Fe_3O_4 (Fig. 4b, d). The $\delta^{13}C$ and $\delta^{2}H$ values of ethane started to decrease with increasing maturity/temperature at 500 °C and 450 °C, respectively.

Actually, isotope rollover of heavy hydrocarbon gases at relatively high thermal maturity is a common phenomenon in both field work and pyrolysis experiments. However, the origin of the isotope rollover has long been debated [35–42]. Our other study will examine the potential mechanism of isotope rollover combined with previously published data in detail and proposed that the decomposition of straight-chain species tightly entrapped in kerogen at high temperature may play a key role [43].

4. Conclusion

Nickel could catalyze the decomposition of organic matter and FTT reactions both in the absence and presence of water. These two kinds of catalytic reactions could cause a substantial increase of methane yield and $\delta^{2}H_{CH4}$ value. The $\delta^{13}C$ value of catalytic methane can be higher or lower than the thermogenic methane, depending on the relative abundance of methane formed via FTT reactions. FTT reactions were an important pathway for methane generation in Ni-catalyzed pyrolysis of organic matter, especially in the presence of water. CO_2 yield and $^{13}C_{CO2}$ value also increased obviously in the presence of nickel due to the catalytic decomposition of organic matter.

The influence of magnetite on gas generation is small. Magnetite could help to oxidize the long-chain hydrocarbons and cause a slight increase of methane yield at high temperature (430–550 °C) and an increase of CO_2 yield at all temperatures in the absence of water. Water inhibit the effect of magnetite on methane and CO_2 generation at relatively low temperature (< 450 °C). The addition of magnetite did not have systematic influence on heavy hydrocarbon gas yield, carbon and hydrogen isotopes of hydrocarbon gases and carbon isotopes of CO_2.

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