Research Article

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Organic-inorganic interactions in the system of pyrrole-hematite-water at elevated temperatures and pressures

Abstract: The distribution and abundance of pyrrolic compounds in sediments and crude oils are most likely influenced by inorganic sedimentary components. In this paper, thermal simulation experiments on the system pyrrole-hematite-water were carried out at elevated temperatures and pressures in order to investigate the effect of organic-inorganic interactions on the preservation of pyrrolic compounds. Compositions of the reaction products were analyzed with GC-MS and GC-FID methods. In the closed system pyrrole-hematite-water, the nitrogen-oxygen exchange obviously occurred at temperatures above 350°C in accordance with the thermochemical calculation. Large amounts of furan and ammonia were generated after simulation experiments, indicating that the conversion of pyrrole into furan was the dominant reaction. Thermochemical exchange effect between organic nitrogen and inorganic oxygen was obviously facilitated by elevated temperatures and found to be catalyzed by hematite, but inhibited by the increasing volume of water. Thermodynamically water spontaneously reacts with pyrrole above 300°C. The reaction of pyrrole-hematite-water is an exothermic process in which the reaction heat positively correlates with temperature. The heat released was estimated as 9.0 KJ/(mol) pyrrole - 15.0 KJ/(mol) pyrrole in typical oil reservoirs (100°C–150°C) and 15.0–23.0 KJ/(mol) pyrrole in typical gas reservoirs (150°C–200°C). The calculated activation energy of the nitrogen-oxygen atom exchange is about 129.59 kJ/mol. According to the experimental results, a small amount of water may effectively initiate the nitrogen-oxygen exchange. The study would improve our evaluating of the preservation and fate of pyrrolic compounds in deeply buried geologic settings and further understanding of thermochemical processes behind the degradation of petroleum.

1 Introduction

Pyrrolic compounds in sediments and crude oils are characterized with abundant geological and geochemical information, and nowadays have gained wide attention in geochemistry. Geological factors affecting the distribution and abundance of pyrrolic compounds have been traditionally related to palaeoenvironment of deposition [1–3], thermal maturity [4–9] and source characteristics [1, 4, 10], as well as to migration effects [11–16]. In the last two decades, however, geochemists have increasingly recognized that water [17–20] and inorganic minerals [21–26] may participate as reactants or catalysts in the formation and compositional evolution of petroleum. These findings strongly suggest that organic-inorganic interactions may also have implications for the fate and preservation of pyrrolic compounds in sedimentary basins. Throughout the generation, expulsion, migration, and accumulation processes, pyrrolic compounds are potentially exposed to various quantities of natural inorganic fluids and metal oxides in migration conduits and reservoirs. Because the nitrogen atom is more electronegative than the carbon atom, it creates an active site on the molecules of nitrogen compounds and enhances their polarity. As a result, pyrrolic compounds may be highly reactive to inorganic sedimentary ingredients in deep burial geological settings. Up to now little work has been carried out on the influence of inorganic sedimentary components on the preservation of pyrrolic compounds.

In consideration of the complexity of the fate of organic nitrogen compounds in geologic settings and the ne-

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cessity of exploring new identifying indices of oil and gas accumulation in high- to over-mature source rocks, a series of thermal simulation experiments have been carefully designed. The designed experiments allow the reaction of pyrrole with water and hematite to occur under a thermal regime in which N-O atomic exchange is the dominant reaction, while thermal cracking of organic N compounds is minimized. In the present study, pyrrole, the simplest pyrrolic compound, was used as a model nitrogen compound.

Thermochemical atom exchange between organic nitrogen and inorganic oxygen was shown to occur in the system pyrrole-hematite-water at elevated temperatures and pressures under laboratory conditions. Based on detailed analyses, the thermodynamic characteristics and the kinetics of the above system had been tentatively discussed. New insights into the preservation of pyrrolic compounds under geological circumstances are given from the perspective of organic-inorganic interactions, which may contribute to reappraisal of the geochemical cycle of nitrogen in sedimentary reservoirs.

2 Experimental

Pyrrole utilized in the experiments and furan used for gas chromatograph analysis are analytical pure, purchased from Sigma-Aldrich and Farco chemical supplies. Hematite (Fe_2O_3) was obtained from Asia Pacific Suppliers. Thermal simulation experiments on the pyrrole-hematite-water system were carried out using an autoclave at high temperatures and high pressures. The autoclave was a vertical reactor made of a stainless-steel tube with a volume of 200 mL. Each runtime, 0.1 g of hematite powder was placed on the bottom of the reactor, then air from the reactor was removed under vacuum, 10.0 mL of pyrrole and 10.0 mL of distilled water were loaded into the autoclave through a feed regulator of the autoclave. For study of kinetics, the designed temperature programme is applied in the present experiments. The reactor was first heated to 300°C directly and then to 350°C, 375°C, 400°C, 425°C and 450°C following a program of different heating times of 360 h, 288 h, 216 h, 144 h, 72 h, respectively. Because at the same reaction time higher temperature generally results in higher conversion of the reaction, shorter duration of experiment at higher temperatures or longer duration of experiment at lower temperatures is therefore utilized in the experiments in order to obtain a rational distribution of kinetic data. Temperature was controlled to within 1°C of the set value, and was monitored using a pair of ther-
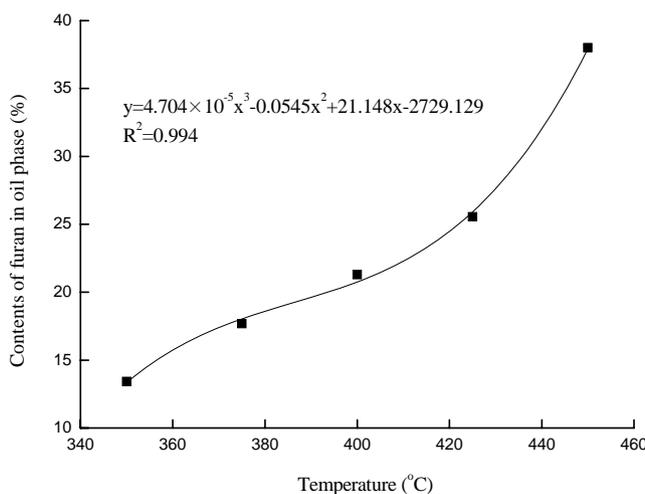
mocouples secured to the outer and inter walls of the autoclave. The final pressure of the reaction system ranged from 6.0 MPa to 10.0 Mpa. When the desired reaction temperature or time was reached, the stainless steel autoclave was withdrawn from the oven, air cooled for 30 min, and then rapidly cooled to room temperature by quenching in water. The mixture of oil and water was drawn from the autoclave with a pipette and separated with a micro extraction funnel.

The oily products were analyzed on an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a HP 5970 mass selective detector (Hewlett-Packard, Palo Alto, CA, USA). The gas chromatograph was equipped with two detectors, a thermal conductivity detector and a flame ionization detector; five different columns, 3 RTX-65TG capillary columns (high polarity phase; Crossbond diphenyl dimethyl polysiloxane; 30 m × 0.25 mm i.d., film thickness 0.1 µm) and 2 packed columns (stainless steel column packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport; 30 m × 0.32 mm i.d., film thickness 0.25 mm). The identification of peaks was achieved by comparing their retention times with those of standards purchased from Nu Chek Prep (Elysian, MN, USA) and Sigma-Aldrich (Sigma, St. Louis, MO, USA) under the same gas chromatography conditions. Peaks were integrated using Hewlett-Packard Chem Station software. The oven temperature was programmed as follows: after the oven temperature was kept at 40°C for 10 minutes, it was heated to 60°C with a heating rate of 0.5°C/min and stayed at this temperature for 15 minutes, then reached 180°C with a heating rate of 5.0°C/min and stayed at this temperature for 3 minutes. The detector temperature was set at 250°C. N_2 is used as carrier gas. Mass spectra were obtained at 70 eV in the electron impact ionization mode; the spectrometer was operated in the full scan mode over the mass range from m/z 50 to 200 and spectral data were acquired at a rate of 4.7 scans/s. The source and quadrupole temperatures were maintained at 230°C and 150°C, respectively. Total ion current chromatograms were acquired and processed using G1701DA D.01.02 Standalone data analysis software (Agilent Technologies) on a Pentium IV computer that was also used to control the whole system.

Measurements of products in aqueous phase were carried out using Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a FID system and Agilent headspace G1888 autosampler (Wilmington, DE, USA). GC conditions were as follows: a J&W capillary column DB-ALC1 (30 m × 0.32 mm i.d., film thickness 1.8 µm; Wilmington, DE, USA) at 90°C, the initial high purity nitrogen carrier gas flow rate of 3.8 mL/min at
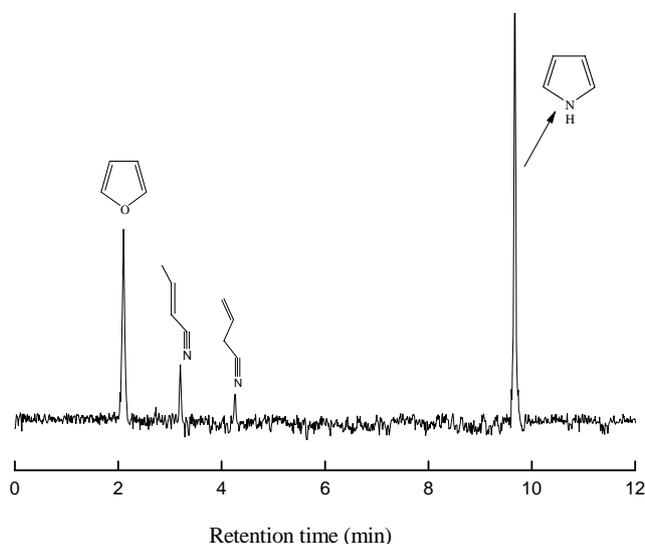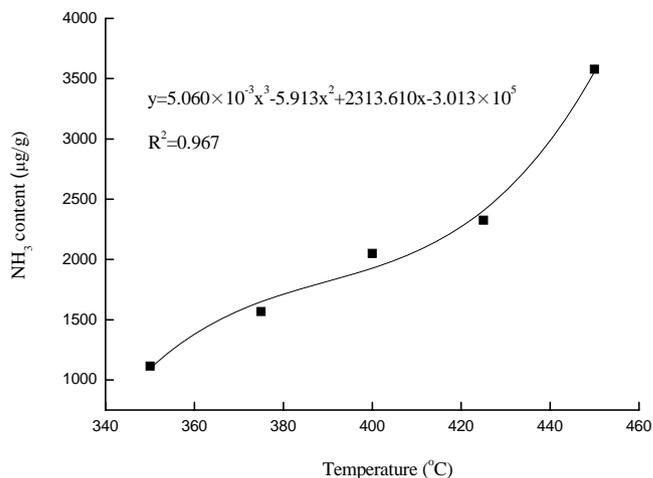
Figure 1: Total ion chromatogram for organic products in the pyrrole-hematite-water system (450°C).

Figure 2: Contents of furan in oil phase with different temperatures.

Figure 3: Effect of the reaction temperature on the content of ammonia from headspace - gas chromatography analysis of aqueous products.

the initial pressure of about 1.86×10^4 Pa. The inlet temperature was 150°C with a split ratio of 20:1. The column oven temperature was initially set at 35°C for 15 min, and then it ramped to 200°C at 25°C/min and held at 200°C for 5.4 min. The flame ionization detector temperature was 250°C, and the hydrogen and air flows were 30 mL/min and 400 mL/min, respectively. Headspace operating conditions were as follows: 30 min with strong shaking for the sample equilibration at a temperature of 90°C, the temperatures of the sample loop and the transfer line were 115°C and 120°C, respectively. The injection time was 1.0 min, and the loop fill and equilibration times were 0.2 min and 0.05 min, respectively. The vial pressure was 9.65×10^4 Pa and vial pressurization time is 0.2 min. The sample prepa-

ration and measurement procedures were as follows: Inject 1 mL of aqueous products into a closed 25 mL vial by microsyringe and place the vial in the headspace sample tray for headspace GC measurements.

3 Results and discussion

3.1 Analysis of the reaction products

Products in oil phase were characterized with gas chromatography-mass spectrometry (GC-MS). The typical total ion chromatogram for oily products was shown in Figure 1. Furan and pyrrole were found to be two dominant species in the oily phase (Fig. 1). Besides the peaks of furan and pyrrole, two small peaks of 2-butenenitrile (RT = 2.1017 min) and 3-butenenitrile (RT = 4.2584 min) also appeared in the total ion chromatogram. The formation of 2-butenenitrile and 3-butenenitrile was attributed to ring-opening reactions associated with pyrrole, and determined as high-temperature byproducts of the pyrrole-hematite-water system. There was a positive relationship between contents of furan and temperatures, which could be described by the cubic function $y = 4.704 \times 10^{-5} x^3 - 0.0545 x^2 + 21.148 x - 2729.129$ (Fig. 2).

Aqueous products were analyzed using headspace - gas chromatography (HS-GC). It was illustrated in Figure 3 that at 350°C–450°C, ammonia was obviously generated in the aqueous phase and its content increased with the increasing temperature. High temperature was obviously favorable to the production of ammonia and furan. Based

**Table 1:** The thermodynamic data for the pyrrole-hematite-water system.

Species	$\Delta_f H_m^\theta$ (kJ·mol⁻¹)	$\Delta_f G_m^\theta$ (kJ·mol⁻¹)	$\Delta_f S_m^\theta$ (J·mol⁻¹·K⁻¹)	$C_{p,m}^\theta$ (J·mol⁻¹·K⁻¹) a	b×10²	c×10⁶	d×10⁷
C_4H_5N (l)	63.1	160.3	156.4	37.545	64.459	1680	17.8
C_4H_4O (l)	−62.3	0.90	177.0	33.281	65.201	2220	31.2
H_2O(l)	−285.84	−237.19	69.94	29.160	1.449	−2.02	0
NH_3(g)	−46.19	−16.63	192.51	25.895	3.300	−3.046	0

Notes: $\Delta_f H_m^\theta$, standard enthalpies of formation; $\Delta_f G_m^\theta$, standard Gibbs energy of formation; $\Delta_f S_m^\theta$, standard entropy; $C_{p,m}^\theta$ heat capacity; a, b, c and d, parameters for heat capacity; $C_{p,m} = A + bT + cT^2 + dt^3$
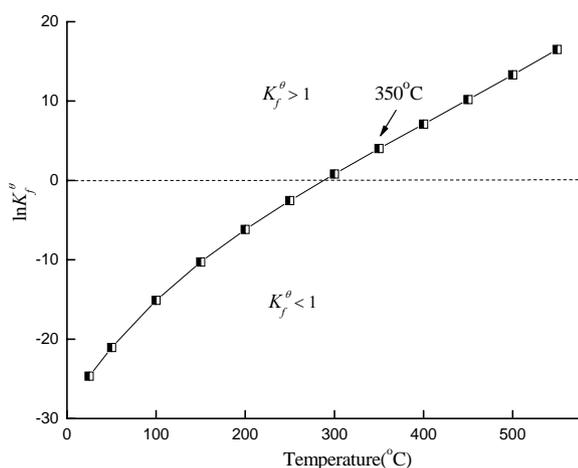
Figure 4: Effect of temperature on the standard equilibrium constant K_f^θ.

on the analysis of the oil-water 2-phase products, furan and ammonia were determined as the two main products of the pyrrole-hematite-water system. It should be noted that the reaction between pyrrole and water was very slow or inhibited at temperatures below 100°C. Even in the presence of hematite, furan and/or ammonia were hardly detected below 200°C using the present analytical methods. The reason should be attributed to the high reaction activation energy associated with the high stability of pyrrole molecule. Thermally pyrrole ring is very stable due to its high decomposition (above 650°C) [27]. Long-term lower-temperature simulation experiments are impossible in the laboratory and thermal experimental studies have to be time limited. To realize the reaction of pyrrole and water, it is necessary to further increase the simulation temperature in the laboratory which inevitably exceeds range of temperatures of typical oil & gas reservoirs ($\leqq$ 200°C). In the simulation experiments, in the presence of hematite the conversion of pyrrole into furan evidently occurred at 350°C, and the corresponding conversion was 13.43%. When reaction temperature increased to 400°C, the con-

version of pyrrole in the present system reached 21.29% which was much higher than the conversion of the pyrrole-water system (3.01%). It was concluded that hematite had played a catalytic role in the thermochemical atom exchange between organic nitrogen and inorganic oxygen. The reaction pathway could be written as followed,

$$ \text{(pyrrole)} + H_2O \xrightarrow{Fe_2O_3} \text{(furan)} + NH_3 \qquad (1) $$
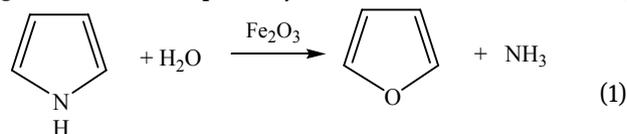
According to the literature data on simulation of hydrocarbon generation, the 1.6–2.3% vitrinite reflectance values of source rocks are attained at temperatures of about 350°C–450°C, which correspond to the temperatures of 110°C–140°C in geological settings [28–30].

3.2 Thermodynamics

In the analysis of a chemical reaction, the associated chemical equilibrium for the reaction may be used in preliminary work to determine if a reaction is thermodynamically favorable at a given temperature. If the equilibrium constant K is > 1 (or log (K) > 0), the reaction goes to the right and the thermodynamics for the reaction are favorable. On the other hand, if the equilibrium constant K is < 1 (or log (K) < 0), the reaction goes to the left and the thermodynamics for the reaction are not favorable. Thermodynamics of the pyrrole-hematite-water system was discussed based on the reaction pathway (1). To determine the change in the chemical equilibrium for the above reaction, the effect of temperature on the standard equilibrium constant K_f^θ was calculated and shown in Figure 4. Thermodynamic data used in this and subsequent calculations are listed in Table 1 [31]. In Figure 4, from 25°C to 550°C the value of K_f^θ increased with the increase of temperature, which implied that the increasing temperature thermodynamically favors the reaction of pyrrole-
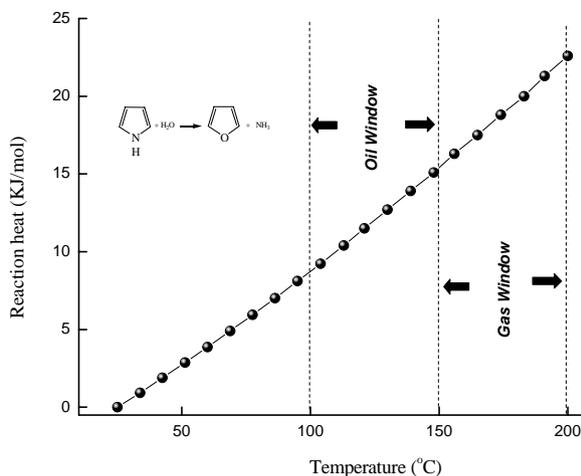
Figure 5: Simulation results of the relation between the reaction heat and temperature.
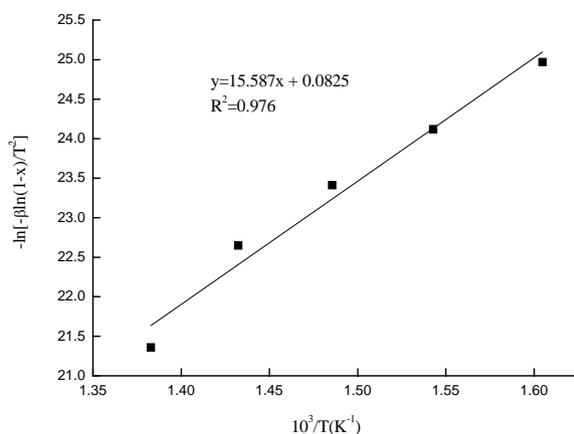
Figure 6: The regression line for the reaction between pyrrole, hematite and water.

hematite-water. Especially when T > 300°C, $K_f^\theta > 1$ and the reaction of pyrrole-hematite-water could proceed spontaneously.

Calculations of the reaction heat for the overall pyrrole-hematite-water system were performed by the use of HSC chemical software 5.0 developed by Outokumpu Research Oy and illustrated in Figure 5, which was based on the principle of the Gibbs free-energy minimization. The data presented in Figure 5 indicated that the reaction of pyrrole-hematite-water was an exothermic process in which the reaction heat positively correlated with temperatures (Fig. 5). The heat released was estimated as 9.0 KJ/(mol) pyrrole –15.0 KJ/(mol) pyrrole in typical oil reservoirs (100°C–150°C) and 15.0 KJ/(mol) pyrrole –23.0 KJ/(mol) pyrrole in typical gas reservoirs (150°C–200°C).

3.3 Kinetics

The reaction between pyrrole, hematite and water is assumed as a first-order reaction, and its kinetic equation is written as

$$\frac{dx}{dt} = Ae^{-E/RT}(1-x) \qquad (2)$$

Where x is reaction conversion, t is reaction time, A is the apparent frequency factor, E is apparent activation energy, R is the gas constant, and T is absolute temperature. Considering the constant rate heating condition $\beta = dt/dt$, eq. (3) is obtained

$$\frac{\beta dx}{1-x} = Ae^{-E/RT}dT \qquad (3)$$

The integration of eq. (3) will give eq. (4)

$$\int_0^x \frac{\beta dx}{1-x} = \int_{T_0}^T Ae^{-E/RT}dT \qquad (4)$$

In eq. (4), T_0 is room temperature. Because the rate of the reaction at T_0 is very slow, we have

$$\int_{T_0}^T Ae^{-E/RT}dT = \int_0^T Ae^{-E/RT}dT \qquad (5)$$

Let $u = -E/RT$, then

$$\int_0^T Ae^{-E/RT}dT = \frac{AE}{\beta R}\frac{e^u}{u^2}\sum_{n=0}^{\infty}\frac{(n+1)!}{u^n} \cong \frac{AE}{\beta R}\frac{e^u(u+2)}{u^3} \qquad (6)$$

Combining eq. (5) and eq. (6), the approximate integration of eq. (4) will give

$$\frac{-\ln(1-x)}{T^2} = \frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)e^{-E/RT} \qquad (7)$$

Eq. (7) after taking natural logarithm becomes

$$\ln\left[\frac{-\beta\ln(1-x)}{T^2}\right] = \ln\frac{AR}{E}\left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \qquad (8)$$

As to most chemical reactions, $\frac{E}{RT} \gg 1$, and then $\left(1 - \frac{2RT}{E}\right) \approx 1$. Thus, Eq. (8) can be changed as

$$\ln\left[\frac{-\beta\ln(1-x)}{T^2}\right] = \ln\frac{AR}{E} - \frac{E}{RT} \qquad (9)$$

Based on the conversions at different temperatures, the linear regression coefficients of lines for $-\ln\left[\frac{-\beta\ln(1-x)}{T^2}\right]$ vs. $10^3/T$ were drawn. By using the linear regression of $-\ln\left[\frac{-\beta\ln(1-x)}{T^2}\right]$ vs. $10^3/T$ in Eq. (9), the apparent activation energy E and apparent frequency factor A

were determined by the slope and intercept of regressed line respectively (Fig. 6). The apparent activation energy is 129.59 kJ/mol and apparent frequency factor is 1.44×10^4 s^{-1}. Then, the kinetic model for the reaction between pyrrole, hematite and water can be written as

$$\frac{dx}{dt} = 1.44 \times 10^4 e^{-15587/T} (1 - x) \tag{10}$$

It should be pointed out that hematite potentially may also provide oxygen for the formation of furan. The additional blank tests were carried out using 0.1 g Fe_2O_3 powder and 10.0 mL pyrrole at 350°C–450°C. Properties of the oil-water 2-phase products were analyzed by FT-IR and GC. Furan and ammonia had not been found in the blank tests, which showed that there was no thermochemical atom exchange between hematite and pyrrole in the blank tests. Therefore, the possibility of hematite providing inorganic oxygen in the formation of furan molecule could be precluded in the thermal simulation experiments. The formation of furan and ammonia in the reaction system pyrrole-hematite-water was the result of the nitrogen-oxygen exchange between pyrrole and water. At the same time it must be also noted that the amount of water used in the experiments could greatly affect the scale of the exchange between organic nitrogen and inorganic oxygen. The additional blank tests showed that the increasing amount of water led to the decreasing reaction conversion. So, in the system pyrrole-hematite-water potential catalysis of hematite was believed to be closely associated with the amount of water. The amount of water (10.0 mL) used in the experiments was very small compared with the volume of the reactor (200 mL). In other words, the volume of water accounted for only 5% of the volume of the reactor. When the temperature exceeded 100°C, the small amount of liquid water was vaporized and converted into gaseous water. At this time, from the viewpoint of physical chemistry, water was at a saturated state. According to the previous study [32], water vapor could maximize the number of Lewis acid centers on the surface of hematite and strengthen the surface acidity of hematite. Thus, a small amount of water utilized in the reaction system was changed into water vapor at elevated temperatures, enhancing the catalysis of Fe_2O_3 during the nitrogen-oxygen exchange. Based on the above discussion, it is deduced that the system pyrrole-hematite-water is affected by at least two factors: the catalysis of metal oxides and the amount of water.

It should be also noted that the results of the simulation experiments were obtained in an idealized system which in fact precluded many complex sedimentary factors. There are many potential kinetic factors in geological environments that may enhance or reduce the rate of exchange between organic nitrogen and inorganic oxygen, such as pH, Eh, clay minerals as well as temperature. Although it is now clear that temperature, Fe_2O_3 and a small amount of water may greatly influence the overall reaction rate of nitrogen-oxygen exchange, the effects of geological factors mentioned above still need further investigation. Because the goal of this study was to examine the possibility of the reaction of pyrrole-hematite-water, the design of the experiments was not to evaluate the effect of other geological factors on organic-inorganic interactions between pyrrole and water. Future studies would be required to investigate the other factors in geological environments that may enhance or reduce the rate of exchange between organic nitrogen and inorganic oxygen, which is beyond the scope of this article.

In the present experiments nitrogen-oxygen exchange between pyrrole and water is chemically regarded as a substitution reaction. The amount of water, the presence of hematite and elevated temperatures are experimentally determined as important factors for initiation of the reaction system pyrrole-hematite-water. Geologically organic-inorganic interactions between pyrrolic compounds and water should be considered as a geochemical process which, not only is referred as a chemical reaction but also includes many elementary steps, such as dissolution of reactants, diffusion to the point of reaction, geochemical interaction in the aqueous phase and mineral precipitation. Additionally, physicochemical properties of pyrrole, hematite and water will change with the increasing temperature, which may also to some extent affect the scale of nitrogen-oxygen exchange. Although the present results of the simulation experiments could not yet be directly applied to the geological settings, they are theoretically valuable for presenting us with an important clue to recognize the possibilities of organic-inorganic interactions between pyrrolic compounds and water. The fate and preservation of pyrrolic compounds in deep sediments are most likely influenced by the amount of water and the presence of metal oxides. Incorporation of such factors into geochemical models will further improve prediction of the abundance and the distribution of pyrrolic compounds in natural environments over geologic time. The next work will be focused on the thermochemical exchange between organic nitrogen and inorganic oxygen using more complex pyrrolic compounds, such as carbazoles and benzocarbazoles.

4 Conclusions

1. Furan and ammonia are the two main products of the pyrrole-hematite-water system. Elevated temperatures are obviously favorable to the production of ammonia and furan. The positive relationship between the content of furan and temperature can be described by a cubic function, which was also illustrated in the relationship between the ammonia content and temperature.

2. When the reaction temperature T > 300°C, the value of the standard equilibrium constant $K_f^\theta > 1$. Thermodynamically water spontaneously reacts with pyrrole, which involves a chemical exchange between organic nitrogen and inorganic oxygen.

3. The thermochemical reaction of pyrrole-hematite-water was an exothermic process in which the reaction heat positively correlated with temperature. The heat released was estimated as 9.0 KJ/(mol) pyrrole–15.0 KJ/(mol) pyrrole in typical oil reservoirs (100°C–150°C) and 15.0 KJ/(mol) pyrrole –23.0 KJ/(mol) pyrrole in typical gas reservoirs (150°C–200°C).

4. According to the kinetic model, the calculated activation energy of the nitrogen-oxygen atom exchange is about 129.59 kJ/mol.

5. Hematite plays a role of catalyst in the thermochemical exchange between organic nitrogen and inorganic oxygen. The Lewis acid sites on the surface of hematite are likely catalytic active sites.

6. The system pyrrole-hematite-water is affected by at least two factors: the catalysis of Fe_2O_3 and the amount of water. A small amount of water may effectively enhance the catalysis of Fe_2O_3 during the nitrogen-oxygen exchange.

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