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Effect of inherent and additional pyrite on the pyrolysis behavior of oil shale

Ronghua Gai, Lijun Jin, Jianbo Zhang, Jianyou Wang, Haoquan Hu *

State Key Laboratory of Fine Chemicals, Institute of Coal Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China

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ABSTRACT

The effect of inherent and additional pyrite on oil shale pyrolysis was investigated in a fixed-bed reactor. The results show that at the temperature range of 460–580 °C, inherent pyrite can improve the oil yield, but the additional pyrite promotes the increase of volatiles. The oil and gas yields in oil shale pyrolysis at 500 °C with the addition of 8 wt.% pyrite are 41.7 wt.% and 14.4 wt.% (all in dry and ash-free basis), respectively, increasing by 4.5 wt.% and 3.3 wt.% compared to those from pyrolysis of raw oil shale. However, the additional pyrite has slightly effect on oil yield at higher temperature, but can enhance the gas yield. The results by TG-MS and XRD analyses indicate that the effect of additional pyrite on the pyrolysis behavior of oil shale is related with the pyrite decomposition.

1. Introduction

The increasing demand of energy and the unstable price of crude oil have encouraged some countries to exploit other alternative fossil fuel sources, such as coal, oil shale and oil sand. Oil shale, as one of the largest hydrocarbon reserves in the world, is estimated to be about 400 billion tons of the oil equivalents, almost 3 times as the reserve of crude oil [1].

Oil shale is commonly defined as a sedimentary rock, which contains various amounts of solid organic materials bound dispersedly in a mineral matrix and yielding oil and gases upon heating. Pyrolysis is a conventional method to obtain oil and gas from oil shale. Minerals are known to be of importance in oil shale processing, and many studies on the effect of minerals on oil shale pyrolysis have been carried out by demineralization of shale [2–7], or the pyrolytic behavior of oil shales and their kerogens [8–11].

Pyrite is usually considered to play a catalytic role in coal liquefaction and gasification processes. Great efforts have been put into studying the effect of pyrite on coal liquefaction [12–16]. Garg [17] found both coal conversion and oil yield can be improved with the addition of 10 wt.% pyrite to the feed slurry. Chen [18] investigated the interaction of pyrite with coal organic matrix in pyrolysis and found the initial decomposition temperature of pyrite in coal can decrease by 100 °C compared with the decomposition of pure pyrite in nitrogen. Considering the similarities between coal and oil shale, it is expected that the pyrite also plays a role during the course of oil shale degradation. Metecan [19] studied the effect of pyrite catalyst on the hydroliquefaction of oil shale and thought the pyrite catalyst can increase the conversion of oil shale below 400 °C. Bakr [20] investigated the role of pyrite during the thermal degradation of kerogen and the results showed pyrite can enhance and accelerate the formation of free-radical, which may be attributed to the nascent sulfur produced during the conversion process of pyrite to pyrrhotite. However, few studies on the different effects of inherent and additional pyrite on the pyrolysis behaviors of oil shale were reported. In this work, the pyrolysis of raw oil shale, demineralized oil shale samples and oil shale with additional pyrite were investigated to explore whether the pyrite can promote the conversion of oil shale.

2. Materials and methods

2.1. Materials

The oil shale sample used in this work was collected from Longkou, Shandong province of China. Before pyrolysis experiments, oil shale was ground to below 100 mesh and dried at 60 °C for 24 h under vacuum. All chemicals (HCl, HF and HNO_3) used in this study were of analytical grade. The natural pyrite was checked with X-ray diffraction before use.

To investigate the effect of additional pyrite on the pyrolysis, raw oil shale (OS-R) was mechanically mixed with different amount of the pyrite, and then ground to below 100 mesh. The fisher assay of OS-R, the mineral composition of pyrite and raw oil shale are given in Table 1 and Table 2, respectively.

* Corresponding author. Tel.: +86 411 84986157; fax: +86 411 84986157.
E-mail address: hhu@dlut.edu.cn (H. Hu).

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Table 1
Fischer assay of oil shale.

OS-R	Oil	Char	Water	Gas[a]
Yield (wt.%, d)	16.46	76.97	3.52	3.05

d: dry base.
[a] By difference.

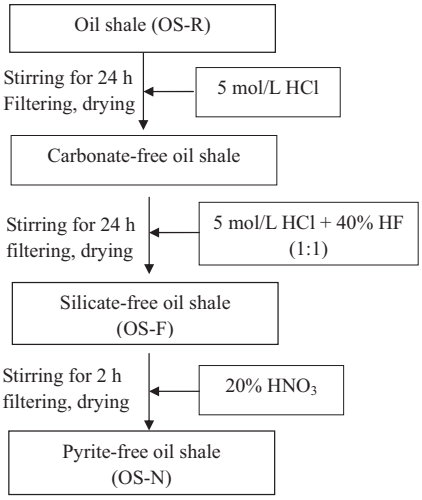

Fig. 1. Demineralization procedure of oil shale.

2.2. Demineralization

Demineralized samples were prepared by washing the OS-R with HCl, HF and HNO_3 solutions in sequence. The procedure was shown in Fig. 1. Typically, about 1 g oil shale sample was stirred with 10 ml acid solution at room temperature, and then the slurry was filtered, washed with deionized water until the filtrate became neutral and dried at 60 °C for 12 h under vacuum after each step. The silicate-free and pyrite-free oil shale samples were expressed as OS-F and OS-N respectively. The proximate and ultimate analyses of raw and demineralized oil shale samples are listed in Table 3.

2.3. TG-MS analysis

TG analysis (TGA) was performed on a Mettler-Toledo TGA/SDTA851[e] analyzer. During the experiment, about 15 mg oil shale sample was placed in a ceramic crucible and heated from 25 to 850 °C under 60 ml/min N_2 atmosphere with a heating rate of 10 °C/min. The evolved gases including H_2S and SO_2 were analyzed by a quadrupole mass spectrometer (Thermostar MS) through a heated capillary transfer line linked to the TG analyzer (TG-MS) under argon atmosphere.

Table 2
Ash composition of raw oil shale and pyrite.

Sample	Component (wt.%)					
	SiO_2	CaO	Fe_2O_3	Al_2O_3	SO_3	Others
OS-R	39.10	30.20	12.70	6.61	5.01	6.38
Pyrite	1.24	–	31.86	0.38	65.99	0.53

Table 3
Proximate and Ultimate analyses of samples.

Sample	Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
	M_{ad}	A_d	V_{daf}	C	H	N	S	O[a]
OS-R	3.44	49.78	78.97	77.32	7.79	1.29	2.53	11.07
OS-F	3.61	5.78	68.70	76.88	8.33	1.62	2.30	10.87
OS-N	6.40	1.46	67.77	73.13	7.97	3.93	1.47	13.50

ad: air dry base; daf: dry and ash-free base.
[a] By difference.

2.4. Pyrolysis in a fixed bed reactor

Oil shale pyrolysis was performed in a vertical fixed-bed reactor. The apparatus and process were described in the literatures [21,22]. The reactor loaded with 5 g sample was heated to the desired temperature (420–620 °C) within 10 min by the preheated furnace and kept for 30 min under 300 ml/min of N_2 as the carrier. The liquid products (oil plus water) were collected by a cold trap after the reactor, and the volume of gas product was measured by a gas flowmeter. The solid char was weighted after experiment. The oil and water were separated by the method of ASTM D95-05[e1] (2005). The oil and gas yield was calculated as the weight percentage of oil and gas, respectively, in the oil shale sample expressed on a dry-ash-free (daf) basis.

2.5. Characterization

The FT-IR spectra of raw and demineralized oil shale samples were recorded from 4000 to 400 cm^{-1} by an EQUINOX55 spectrometer using KBr pellet technique. The weight ratio of oil shale to KBr is about 1:100. The X-ray diffraction (XRD) patterns of pyrite and char samples were obtained on a D/MAX-2400 diffractor with Cu Kα at 40 kV and 40 mA. And the step size is 0.02° and the scan speed is 4°/min.

3. Results and discussion

3.1. Sample characterization

To investigate the effect of inherent pyrite on oil shale pyrolysis, it is necessary to remove other minerals existed in oil shale. Generally, acid treatment using HCl and HF solution is effective for removing most carbonates, oxides, and monosulfide minerals from sedimentary rocks and leaving the kerogen and pyrite largely unaffected [23]. Pyrite can be removed by HNO_3 solution; however, nitric acid, for its strong oxidizing agent, will affect the kerogen by increasing nitrogen and oxygen contents via the introduction of carboxylic groups to the structure of kerogen [2]. Quantitative removal of pyrite without alteration of the organic composition is impossible, but the effect can be minimized by using dilute acid at moderate temperatures for a time as short as possible [24].

The XRD and FT-IR analyses of raw and demineralized oil shale samples are shown in Fig. 2. The XRD patterns show that the major minerals in raw oil shale are calcite, quartz and pyrite. After HCl and HF treatment, calcite and quartz were removed, and the peaks attributed to pyrite are present in OS-F sample. However, the patterns of pyrite disappeared after HNO_3 treatment, suggesting the pyrite was removed. The presence of calcite and quartz in oil shale is also confirmed by FT-IR spectra. It can be seen from Fig. 2b, the sharp bands at 1430 cm^{-1} and 877 cm^{-1} are characteristic of calcite minerals; the sharp bands in the range 1170–1060 cm^{-1} and 804–780 cm^{-1} are attributed to quartz. The bands at 3000–2850 cm^{-1} present in three samples are due to the asymmetric and symmetric C—H stretchings of methylene groups. In the spectra of OS-F and OS-N samples, the band at 1600 cm^{-1} is associated with aromatic ring stretching vibrations, and the band near 1700 cm^{-1} is related to C=O stretching of carbonyl and/or carboxyl groups. The band located at 3350 cm^{-1} is contributed to OH stretching vibration. The stability of the C=O band in the IR spectra of OS-F and OS-N samples suggests that the chemical