

矿物组成对油页岩超临界水改质产物的影响机制

——以鄂尔多斯盆地长庆油田与黄县盆地龙口地区油页岩为例

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摘要:为阐明矿物组分差异对油页岩超临界水(SCW)原位改质过程中产物生成路径的影响机制,研究选取鄂尔多斯盆地长庆油田(样品CQ,富黄铁矿)和黄县盆地龙口地区(样品LK,富方解石)两类典型油页岩样品,在温度为400℃、压力为25 MPa的超临界水环境下开展高温、高压热模拟实验。综合利用X射线衍射(XRD)、气相色谱(GC)、傅里叶变换红外光谱(FT-IR)和气相色谱-质谱联用(GC-MS)等微观表征手段,深入剖析了气-液-固三相产物的演化规律与差异特征。研究结果表明,矿物基质的差异会影响油页岩SCW改质反应路径:样品LK中高含量的方解石(53.0%)在超临界水环境中发生强烈溶蚀分解反应,释放大量CO₂(占总气量的55.94%),该过程抑制了水-煤气变换反应,导致H₂产率受限(产率仅为10.01%),液体产物呈现“高沥青质(沥青质含量42.18%)、低芳香度(芳烃含量18.89%)”的特征。样品CQ中富含黄铁矿(含量25.5%),在SCW环境下,通过氧化还原反应原位生成磁黄铁矿、磁铁矿和硫等活性相,不仅可以释放酸性组分促进有机质裂解,还可以通过活性相促进甲烷化与加氢反应,使得CH₄与H₂产率大幅提升(产率分别为32.52%和18.88%);其液体产物表现出显著的轻质化特征,沥青质含量降至35.32%,芳烃(含量23.83%)及低碳数烃(碳数≤16)含量显著增加。该研究明确了“矿物-流体-有机质”的协同演化机理,证实了方解石的“溶蚀-CO₂抑制”效应与黄铁矿的“酸性-加氢”效应是影响油页岩SCW改质路径的两个关键因素,为不同矿物类型油页岩差异化原位开采策略的制定提供了重要理论支撑。

关键词:轻质化;油组分;气体分异;矿物-流体相互作用;超临界水改质;油页岩

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Effects of mineral composition on product distribution during supercritical water upgrading of oil shale: A case study of oil shales from Changqing oilfield in Ordos Basin and Longkou area in Huangxian Basin

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Abstract: To elucidate the mechanism by which differences in mineral composition influence product generation pathways during in-situ upgrading of oil shale in supercritical water (SCW), two representative oil shale samples, one from the Changqing oilfield in the Ordos Basin (sample CQ, pyrite-rich) and the other from the Longkou area in the Huangxian Basin (sample LK, calcite-rich), were selected and subjected to high-temperature and high-pressure thermal simulation experiments under SCW conditions at 400 °C and 25 MPa. A combination of X-ray diffraction (XRD), gas chromatography (GC), Fourier transform infrared spectroscopy (FT-IR), and gas chromatography-mass spectrometry (GC-MS) was employed to investigate the evolution behavior and compositional characteristics of gaseous, liquid, and solid products. As indicated by the research results, differences in mineral matrix significantly influence the reaction pathways of oil shale upgrading in SCW. The abundant calcite (53.0%) in the sample LK underwent extensive dissolution and decomposition under SCW conditions, releasing large amounts of CO₂ (accounting for 55.94% of the total gas yield). This process inhibited the water-gas shift reaction, resulting in a low H₂ yield (only 10.01%).

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Consequently, the liquid products exhibited characteristics of high asphaltene content (42.18%) and low aromatic content (18.89%). In contrast, the pyrite-rich sample CQ contained abundant pyrite (25.5%), which was transformed into reactive phases, including pyrrhotite, magnetite, and elemental sulfur through in-situ redox reactions under SCW conditions. These reactive phases not only released acidic components that promoted organic matter cracking, but also enhanced methanation and hydrogenation reactions. As a result, the yields of CH_4 and H_2 increased substantially, reaching 32.52% and 18.88%, respectively. The resulting liquid product exhibited pronounced lightening characteristics, with the asphaltene content decreasing to 35.32% while the contents of aromatic fractions (23.83%) and low-carbon-number hydrocarbons (carbon number ≤ 16) increasing significantly. This study delves into the synergistic co-evolution mechanism among minerals, fluids, and organic matter, and demonstrates that the “dissolution- CO_2 inhibition” effect of calcite and the “acidification-hydrogenation” effect of pyrite are the two key factors controlling the upgrading pathways of oil shale in SCW. These findings provide important theoretical support for developing differentiated in-situ recovery strategies for oil shales with different mineralogical compositions.

Key words: light hydrocarbon enhancement, oil composition, gas differentiation, mineral-fluid interaction, supercritical water upgrading, oil shale

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油页岩作为重要的非常规油气资源,其富含的有机质既是油气生成的物质基础,也是页岩油气的核心赋载体^[1-9]。当储层埋藏至一定深度后,有机质在热力作用下发生热降解反应,生成油、热解气和半焦^[10-16]。除有机质外,油页岩还含有石英、长石、黏土矿物和黄铁矿等无机矿物,这些矿物组分共同构成了致密的储层基质^[17-20]。然而,受油页岩基质致密和孔喉细微的制约,储层内流体传质过程受阻,导致原位油气高效开发面临巨大挑战^[21,25]。为突破这一技术瓶颈,原位热转化技术(in-situ conversion process, ICP)应运而生,目前已成为实现油页岩资源增储上产的关键技术路径^[26-28]。该技术的加热方式主要包括电加热、流体加热、辐射加热和燃烧加热等^[29]。在众多加热介质中,超临界水(supercritical water, SCW)凭借高扩散性、高传质性和低黏度等独特的物理化学性质,不仅能够有效促进有机质热解,还可以提升流体渗流效率,因此在油页岩原位开发中展现出显著的技术优势。

SCW 是指温度与压力均超过临界点(温度为 374.0 °C、压力为 22.1 MPa)的特殊状态的水,其介电常数较低,且密度、黏度等性质可通过调控温压灵活调节,兼具气体的扩散性与液体的溶解能力^[30-31]。研究表明,超临界水特殊的理化性质,使其在油页岩改质过程中发挥多重关键作用:作为反应介质,可溶解分散干酪根以提升反应效率^[31-32];作为反应物,能够参与水解

和加氢反应,提供氢源,同时可借助活性氢抑制结焦、促进重质组分向轻质烃转化,优化生烃品质^[33-36];作为反应性溶剂则可降低反应活化能,促进化学键的断裂与重组^[37-39]。在储层孔隙演化层面,油页岩热解生成的油气会对基质产生“撑开作用”以扩大原有孔隙^[40-41],且矿物分解转化会释放空间形成新孔隙通道^[42-45]。同时,超临界水与超临界 CO_2 作为高密度、低界面张力流体,可共同溶蚀油页岩中的硅酸盐和碳酸盐等矿物,进一步扩孔造缝、降低储层非均质性,为油气运移提供通道^[46-54]。

SCW 特有的高溶解性、扩散性和反应活性的特征,能够高效加热储层,促进油页岩原位裂解并定向生成轻质油气,进而实现超临界混相驱,提升油气采收率^[55-57]。然而,现有研究多聚焦于超临界水对重油的单一改质作用与效果^[46,58-59],对于储层矿物、有机质与超临界水 3 者间的协同演化机制尚不明晰^[60]。尤为关键的是,目前对不同矿物组分(如碳酸盐岩与富黄铁矿页岩)在超临界水环境下的化学行为特征及其对产物生成路径影响的相关研究仍较为匮乏,亟待系统深入探究。

基于上述研究的不足,本文选取矿物组成差异显著的鄂尔多斯盆地长庆油田(富黄铁矿型)与黄县盆地龙口地区(富方解石型)油页岩为研究对象,采用高温、高压釜热模拟的实验方法,系统对比了两种油页岩在

SCW 环境下的产气与排油特征。从“矿物-流体”相互作用的角度,深入探究了方解石溶蚀反应和黄铁矿氧化还原反应对气、液产物组分的影响机理,厘清了甲烷、氢气及复杂液态烃的生成路径,为油页岩 SCW 原位转化的选区评价与工艺参数优化提供科学理论支撑。

1 超临界水热解技术及油页岩特性

油页岩热解技术的核心是通过热解作用将干酪根转化为液态或气态烃类^[61-64]。根据反应体系的不同,该技术可分为无水热解技术、近临界水热解技术和 SCW 热解技术 3 类^[65-67]。其中,SCW 具有高扩散性、高溶解性、高反应活性以及可以与有机物及气体组分完全互溶等独特性质^[68]。研究表明,SCW 不仅可作为反应溶剂,还能作为供氢溶剂直接参与干酪根的转化反应,有效促进重油轻质化过程,从而在较低技术经济成本下提高油页岩转化效率^[34,69-73]。在 SCW 环境下,油页岩中有机质的分解产物主要包括油、气、焦炭和水(图1)。

2 样品选择与实验方法

2.1 实验样品

样品选取两类矿物组成差异显著的典型油页岩:① 样品 LK 取自山东龙口地区,为高方解石含量的灰质油页岩;② 样品 CQ 取自长庆油田三叠系延长组 7 段,为富含黄铁矿的长英质油页岩。全岩 X 射线衍射(XRD)分析结果表明(表1),样品 LK 富含碳酸盐矿物,方解石含量高达 53.0%,石英(含量 25.0%)、黏土

矿物(含量 11.5%)和方沸石(含量 6.4%)含量依次递减,黄铁矿含量极低,仅为 0.4%;样品 CQ 则以石英、黄铁矿和黏土矿物为主要组成成分(含量分别为 45.9%、25.5%和 13.0%),未检测到方解石,其余组分依次为斜长石、方沸石和钾长石(含量分别为 8.3%、5.7%和 1.6%)。

热解数据分析显示(表2),样品 LK 的最高热解峰温($T_{\max}$)为 436 °C,氢指数(HI)为 1 202.1,氧指数(OI)为 11.0,母质类型指数 $[S_2/S_3]$,其中 S_2 为干酪根高温热裂解产生的烃类总量, S_3 为热解阶段含氧化合物(CO_2 和 CO)的释放量]为 109.3;样品 CQ 的 $T_{\max}$ 为 442 °C,HI 为 1 179.0,OI 为 12.8, S_2/S_3 为 92.1。根据《烃源岩地球化学评价方法》(SY/T 5735—2019)中烃源岩有机质类型划分标准,样品 LK 和样品 CQ 的有机质类型均为 I 型,具有高生油潜力,且 $T_{\max}$ 和 HI 等参数数值接近,表明二者有机质的含量、成熟度、生油潜力和母质类型等属性相似,这为对比矿物组分的影响提供了基础条件。

2.2 实验装置与流程

实验采用高温、高压反应釜装置(图2),该装置主要由反应釜本体、智能控制器、压力表、防爆阀、取样接口、集气袋和配套产物检测仪器(气相色谱仪、气相色谱-质谱联用仪和红外光谱仪)组成。具体实验流程如下:① 将油页岩样品经线切割加工为 2 cm × 5 cm (直径 × 高度)的柱状试样,将其与蒸馏水按 1:3.5 的体积比加入反应釜内胆,确保蒸馏水完全浸没样品;② 将内胆装入反应釜并密封后,向釜内通入氮气至压力为 5 MPa,随后快速释压至 1 MPa;重复该充气—放气操作 5 次,以充分置换釜内空气,建立稳定的氮气保护气氛;③ 通过智能控制器设定升温程序,将釜内温

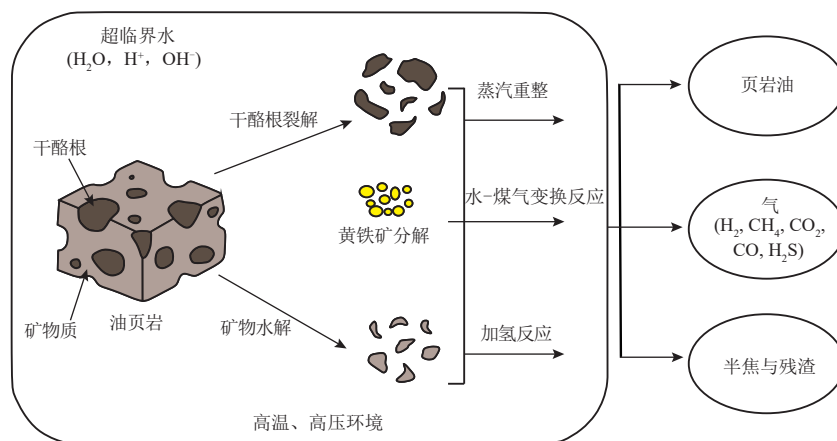


图1 超临界水条件下油页岩热解反应模型

Fig. 1 Conceptual model of oil shale pyrolysis under supercritical water (SCW) conditions

表1 黄县盆地LK与鄂尔多斯盆地CQ油页岩样品XRD矿物组分测定结果

样品名称	矿物组分含量/%						
	石英	钾长石	斜长石	方解石	黄铁矿	方沸石	黏土矿物
LK	25.0	1.0	2.7	53.0	0.4	6.4	11.5
CQ	45.9	1.6	8.3	0	25.5	5.7	13.0

表2 黄县盆地LK与鄂尔多斯盆地CQ油页岩样品地球化学参数

样品名称	$T_{\max}/^{\circ}\text{C}$	HI	OI	S_2/S_3	TOC/%	有机质类型
LK	436	1 202.1	11.0	109.3	11.8	I 型
CQ	442	1 179.0	12.8	92.1	11.4	

注: $T_{\max}$ 最高热解峰温; HI 氢指数; OI 氧指数; S_2/S_3 母质类型指数, 其中 S_2 为干酪根高温热裂解产生的烃类总量, S_3 为热解阶段含氧化合物(CO_2 和 CO)的释放量; TOC 总有机碳含量。

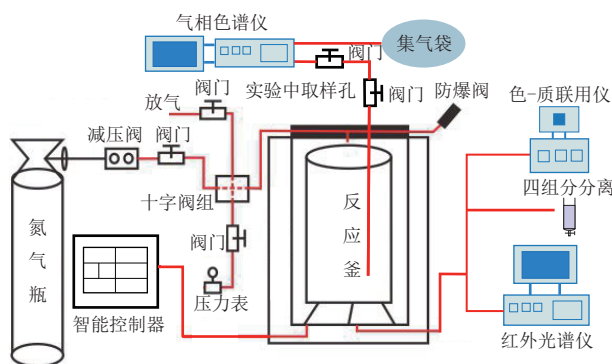


图2 高温、高压实验装置示意图

Fig. 2 Schematic diagram of the high-temperature and high-pressure experimental apparatus

度逐步升至 400°C , 达到目标温度后恒温 400 min , 确保油页岩样品在设定温、压条件下充分发生热解转化反应; ④ 实验结束后, 关闭加热系统。待反应釜自然冷却至室温后, 先通过集气袋收集釜内气体产物; 随后打开反应釜取出内胆, 分别收集液相和固相残渣。

2.3 测试与分析方法

1) 油组分提取: 取实验后液相及固相残渣, 与二氯甲烷-正己烷混合溶剂充分混合, 经超声波振荡充分溶解后, 依次通过过滤和分液操作, 获得固相残渣、水相和油相组分。

2) 组分分离: 称取 30 mg 油样, 依据标准《岩石中可溶有机物及原油族组分分析》(SY/T 5119—2016),

采用柱层析分离法完成饱和烃、芳烃、沥青质和胶质的分离与提纯。

3) 红外光谱分析: 采用 Nicolet iS5 傅里叶变换红外光谱仪 (FT-IR) 对油组分进行测试, 通过光谱特征峰识别样品中的化学键类型与官能团特征, 为探究有机质热解转化规律提供依据。

4) 气相产物检测: 采用安捷伦 6890 型气相色谱仪 (GC), 对收集的气体进行组分定性与含量定量分析, 明确气体产物中各组分的分布特征。

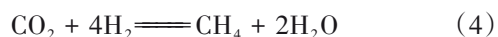
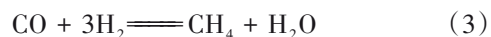
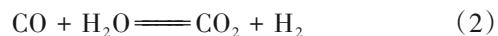
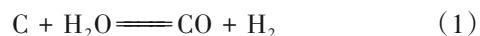
5) 液相产物分子表征: 采用安捷伦 5977+8890 型气相色谱-质谱联用仪 (GC-MS), 对油相产物开展定性与定量分析, 获取油相分子结构和碳数分布规律。

3 结果与讨论

3.1 有机质及矿物的反应机制

3.1.1 有机质热分解作用

有机质反应整体遵循“碳、氢解离—碳、氧重组—碳、氢重构”的转化规律。具体而言, 蒸汽重整反应主导 CO 与 H_2 的生成 [反应式 (1)], 伴随发生的水-煤气变换反应影响体系中的碳-氧平衡 [反应式 (2)], 最终 CO 、 CO_2 和 H_2 进一步发生甲烷化反应 [反应式 (3) 和反应式 (4)], 反应式如下 [74-77]:



3.1.2 矿物反应

石英作为两类油页岩的主要造岩矿物, 在 SCW 条件下化学性质稳定 [78]。其对于干酪根转化的影响主要体现在物理结构层面: 凭借高硬度与热稳定性维持孔隙结构, 防止半焦堵塞孔喉, 为流体渗透与油气运移提供空间 [79]。石英主要发挥物理辅助作用, 本研究 400 min 的充足恒温时间已有效弱化了石英含量差异的影响。

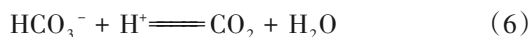
黏土矿物层间域的可交换 H^+ 与金属阳离子可形成弱酸性位点, 选择性催化干酪根 $\text{C}-\text{O}$ 和 $\text{C}-\text{S}$ 等弱键断裂, 促进脱羧和脱硫反应。同时, 较高的孔隙比表面积可吸附自由基并延长寿命, 进而促进二次裂解 [80-81]。本研究中两类样品的黏土矿物均以高岭石

(样品 LK 2.0%, 样品 CQ 2.6%) 和伊/蒙混层(样品 LK 9.2%, 样品 CQ 10.2%) 为主, 伊利石含量较少(样品 LK 0.3%, 样品 CQ 0.2%)。黏土矿物的种类和含量相近, 故黏土矿物的作用强度在两个体系中基本相同。因此, 黏土矿物不是导致样品 CQ 与样品 LK 产物分异的主要影响因素。

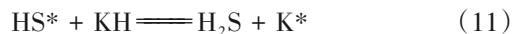
方沸石是两类样品中均含有的少量沸石类矿物, 含量差异较小。在 SCW 条件下, 方沸石仍保留一定的离子交换活性, 可与体系中的 Na^+ 和 Ca^{2+} 等阳离子发生可逆交换, 微弱调控反应体系的酸碱环境^[82]。但方沸石在两类样品中的含量相近且均较低, 在 SCW 条件下性质相对稳定, 且离子交换容量有限, 对反应体系整体 pH 值的波动影响较小, 因此对于干酪根的热解转化过程及最终产物分布的影响较小。

钾长石和斜长石等长石类矿物, 在 SCW 条件下仅发生有限的表面水解溶蚀, 释放少量 K^+ , Na^+ , Ca^{2+} 和 Al^{3+} 等离子^[83]。两类油页岩样品的长石类矿物含量均较低, 且溶蚀速率远低于方解石, 因此既不足以改变干酪根的裂解反应路径, 也不会导致两类样品产物产生明显分异。

样品 LK 中富含的方解石在高温、高压水热体系中极不稳定: 超临界水的离子积较常温显著增大, 可有效促进方解石发生水解反应[反应式(5)]; 同时, 高温环境会诱导体系内盐类矿物发生重结晶, 促使体系中 CO_3^{2-} 与 HCO_3^- 离子浓度升高^[84-85]。上述过程共同形成的酸性水热环境, 进一步推动碳酸氢根分解, 释放大量的 CO_2 [反应式(6)]^[86-88]。



在 400 °C 超临界水环境下, 黄铁矿稳定性较差, 易通过氧化还原反应转化为磁黄铁矿(FeS)和磁铁矿(Fe_3O_4), 并释放出 SO_2 和 H_2 [反应式(7)和反应式(8)]^[89]。同时, 黄铁矿(FeS_2)向磁黄铁矿(FeS)转化的过程中会生成硫[反应式(9)]。干酪根(以 KH 表示, K 代表干酪根骨架, H 为可转移的活性氢)作为氢供体, 与生成的硫发生反应, 生成干酪根自由基(K^*)和硫基自由基(HS^*)[反应式(10)]。生成的硫基自由基(HS^*)继续作为氢受体, 会与其他干酪根分子发生二次反应, 生成硫化氢和干酪根自由基(K^*)[反应式(11)]^[90]。



该过程不仅可以强化超临界水与油页岩体系的溶解性能, 加速有机质热解与生烃, 还可通过释放 H^+ 形成稳定的酸性反应氛围。这种酸性环境一方面可通过质子化作用, 降低干酪根大分子中 $\text{C}-\text{C}$ 键与 $\text{C}-\text{O}$ 键的断裂活化能, 促进有机质深度裂解, 形成更多的短碳链烃类自由基和游离氢^[91-92]; 另一方面可有效促进芳构化与缩合反应, 增加 H_2 的原位供氢来源。同时, 黄铁矿的氧化还原反应可使其表面形成富含硫空位的特殊结构, 这赋予其较强的反应活性: 可将 H_2O 或分子态 H_2 解离为高活性氢离子(H^+), 该活性氢可快速与有机质裂解产生的自由基发生结合反应, 通过这种自由基加氢反应减弱自由基间的缩聚结焦过程, 促进轻质产物的高效生成。此外, 有机质热解过程中伴随的黄铁矿转化及新生硫形成, 可促进干酪根自由基的生成效率, 促进沥青质分解与液态碳氢化合物形成。

3.2 产气特征及差异性

3.2.1 产气组分特征

LK 与 CQ 两个油页岩样品在超临界水热解反应中的产气组分相似, 均包含烃类气体(主要为甲烷、乙烷和丙烷)与非烃类气体(二氧化碳和氢气), 但两种样品的产气组分含量存在较大差异(图 3)。样品 LK 的产气组份中, 烃类气体以甲烷为主(含量 16.24%), 乙烷次之(含量 8.39%), 丙烷及其他烃类组分总含量不足 10.00%; 非烃气体中, CO_2 占总产气量的 55.94%, H_2 仅占总产气量的 10.01%。与之相比, 样品 CQ 的产气组份中, 甲烷仍是烃类气体的主要组分(含量 32.52%), 乙烷次之(含量 14.41%); 非烃类气体中, CO_2 与 H_2 含量趋于相近, 分别占总产气量的 18.77% 和 18.88%。

3.2.2 产气差异性

样品 LK 的 CO_2 产率是样品 CQ 的 2.98 倍, 而其 H_2 产率仅为总产气量的 10.01%。这种“高碳、低氢”的气体分布特征, 主要归因于方解石在超临界水环境下的溶蚀-分解反应及其对水-煤气变换反应的热力学抑制作用。

从矿物溶蚀分解特征来看, 超临界水与方解石可形成 CO_2 -水-方解石协同溶蚀体系。样品 LK 中方解石的溶蚀分解作用促使体系中 CO_2 大量生成。对于 H_2 组分而言, 水-煤气变换反应是其主要来源之一, 而方

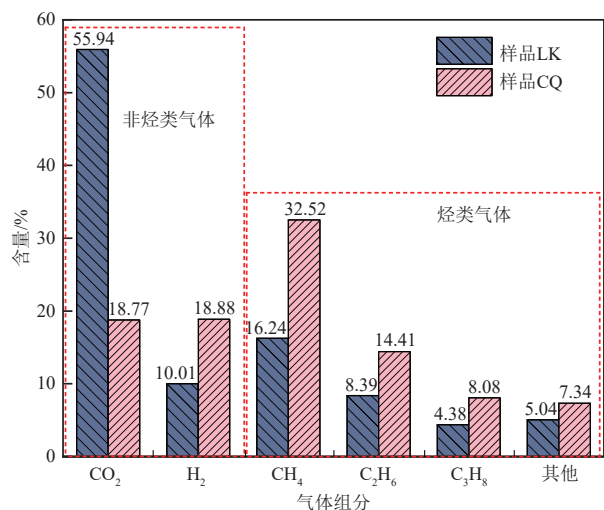


图3 黄县盆地LK与鄂尔多斯盆地CQ油页岩样品超临界水热解反应气体产物中不同组分的气相色谱(GC)分析结果对比

Fig. 3 Comparison of gas chromatographic (GC) results of various components in gaseous products from SCW pyrolysis of LK (Huangxian Basin) and CQ (Ordos Basin) oil shale samples

解石溶蚀释放的高分压CO₂作为该反应的产物,会迫使化学平衡向左(逆向)移动^[93]。此过程影响了水-煤气变换反应的进程,从而使得H₂产率降低,导致样品LK气体产物呈现“低氢气”特征。

结合3.2.1节气体产物分析结果可知,黄铁矿的氧化还原反应产物作为催化剂影响了水-煤气变换反应的平衡;黄铁矿的分解转化不仅抑制了重质组分生成路径,还有效降低了CO₂的过量释放;同时,其释放的活性位点能够促进有机质向H₂和CH₄等轻质气体组分的转化。此外,样品LK产气组分中含有烯烃气体,而样品CQ产气组分中不含烯烃气体。这一差异表明,黄铁矿反应体系促进了样品CQ气体产物的加氢反应,有利于烷烃的生成。

3.3 产出油组分特征

3.3.1 组分特征

超临界水热解反应后油相产物组分含量分析结果如表3所示。其中,样品LK的油相产物组分含量以沥青质(42.18%)和饱和烃(27.69%)的含量最高,芳烃(18.89%)和胶质(11.24%)含量相对较低。样品CQ组分含量以沥青质(35.32%)和芳烃(23.83%)含量最高,胶质(21.70%)和饱和烃(19.15%)含量相对较低。

油页岩SCW改质是一个由矿物、有机质和流体共同参与的复杂多相反应体系。石英、方解石、黄铁矿、

表3 黄县盆地LK与鄂尔多斯盆地CQ油页岩样品超临界水改质后族组分相对含量表

Table 3 Relative group component contents of LK (Huangxian Basin) and CQ (Ordos Basin) oil shale samples after supercritical water upgrading

样品名称	族组分相对含量/%			
	沥青质	饱和烃	芳香烃	胶质
LK	42.18	27.69	18.89	11.24
CQ	35.32	19.15	23.83	21.70

注:此表统计数据依据标准《岩石中可溶有机物及原油族组分分析》(SY/T 5119—2016)测定。

黏土矿物、长石类和方沸石等组分会通过物理作用或化学作用对反应过程产生一定影响。但结合本实验条件与矿物组分定量分析结果,石英、黏土矿物、长石类和方沸石等矿物主要表现为辅助作用,其影响程度远低于方解石的“溶蚀-CO₂抑制”效应与黄铁矿的“酸性释放-原位活性相加氢”效应,且不会导致两类样品产物分布产生明显差异。因此,在本实验设定的温压条件与反应时长下,方解石与黄铁矿是影响两类油页岩SCW改质过程及产物分布的主要矿物。

样品CQ中黄铁矿的存在强化了多环芳烃的解聚作用,促进其生成更多芳香族组分,液相产物的显著轻质化(表现为“低沥青质、高芳香度”特征)。与之相反,样品LK因缺乏有效的黄铁矿-超临界水反应体系,其高分子有机化合物主要发生缩聚和结焦反应,最终导致沥青质含量偏高、油相产物轻质化程度受限。上述差异表明,黄铁矿-超临界水协同反应体系可通过分子重构机制,促进油重质组分向轻质产物的转化。这一机制也解释了样品LK由于缺乏充足的游离氢参与有机质自由基加氢反应,其有机质裂解碎片更易发生缩聚反应,进而生成焦炭或重质油。

3.3.2 碳链差异性

基于热模拟油组分中饱和烃的GC-MS总离子流色谱图,对系列峰进行峰面积积分计算,得到各碳数饱和烃的相对百分含量。结果表明,样品LK和样品CQ经超临界水热解后的油相产物均以正构烷烃为主。样品LK油相产物中正构烷烃碳数主要分布范围为C₁₃—C₂₆,其中C₁₆正构烷烃含量最高(图4)。样品CQ油相产物中正构烷烃碳数主要分布在C₁₄—C₂₆范围内,C₁₇正构烷烃含量最高,且支链烷烃含量相对较低(图5)。

黄铁矿反应体系与超临界水环境通过“解聚促进-缩聚抑制”的双重作用机制,影响液相产物组分分

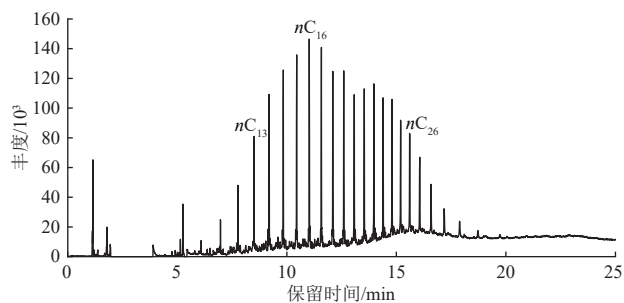


图4 黄县盆地样品LK超临界水热解反应油相产物中饱和烃组分的气相色谱-质谱联用(GC-MS)总离子流色谱图

Fig. 4 Total ion current chromatogram of saturated hydrocarbon fractions in oil-phase products from SCW pyrolysis of LK oil shale sample from the Longkou area in the Huangxian Basin

nC_{13} , 碳原子数为13的正构烷烃; nC_{16} , 碳原子数为16的正构烷烃; nC_{26} , 碳原子数为26的正构烷烃

布^[87]。该碳数分布模式表明,超临界水的强溶解能力促进了中-高碳数碳链(C_{16+})的活化;黄铁矿原位生成的活性相诱导中等碳链组分深度裂解为低碳数轻质组分(碳数 ≤ 16)。高分子有机化合物作为沥青质的主要构成组分^[88],在该体系中易发生解聚反应,且黄铁矿转化提供的活性位点,可进一步加速其裂解为小分子链状化合物。

图6对比了样品LK和样品CQ油相产物中正构烷烃的碳数分布特征及其丰度差异。碳数 ≤ 16 的轻质组分在样品CQ油相产物中含量为30.03%,在样品LK油相产物中含量为26.58%,前者含量略高,说明样品CQ油相产物中低碳数正构烷烃含量更高。16<碳数 ≤ 21 的中质组分在样品CQ油相产物中含量为41.86%,在样品LK油相产物中含量为34.81%,前者

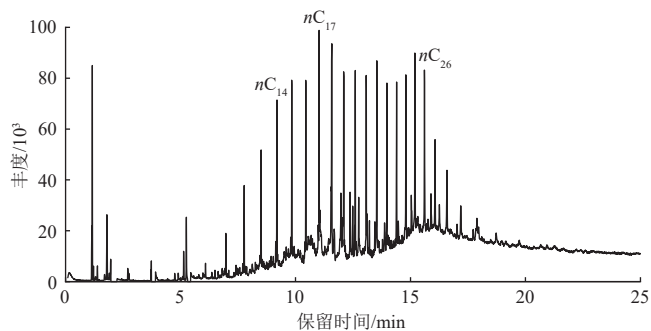


图5 鄂尔多斯盆地样品CQ超临界水热解反应油相产物中饱和烃组分的气相色谱-质谱联用(GC-MS)总离子流色谱图

Fig. 5 Total ion current chromatogram of saturated hydrocarbon fractions in oil-phase products from SCW pyrolysis of CQ oil shale sample from the Changqing Oilfield in the Ordos Basin

nC_{14} , 碳原子数为14的正构烷烃; nC_{17} , 碳原子数为17的正构烷烃; nC_{26} , 碳原子数为26的正构烷烃

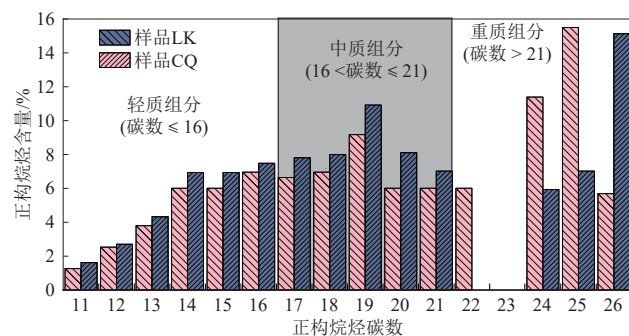


图6 油页岩样品超临界水热解反应油相产物中不同碳数饱和烃组分相对百分含量分布柱状图

Fig. 6 Histogram of relative percentage distribution of saturated hydrocarbon components with different carbon numbers in oil-phase products from SCW pyrolysis of oil shale samples

含量显著更高,说明样品CQ油相产物中以中碳数正构烷烃为主要组分。碳数 > 21 的重质组分在样品LK油相产物中含量为38.61%,在样品CQ油相产物中含量为28.11%,前者含量更高,说明样品LK油相产物中高碳数正构烷烃分布特征更为突出。结合组分分析结果(表3)可知,样品CQ油相产物中沥青质含量低于样品LK。这一现象表明,在超临界水热解体系中,黄铁矿反应体系有利于有机质大分子中支链的断裂,同时可以促进重质组分(如沥青质)的裂解,进而提高轻烃组分的相对含量;而样品LK因黄铁矿含量较少,缺乏这一有效的促进作用,导致其油相产物中重质组分含量较高,轻质组分含量相对较低。

3.3.3 官能团反应机理

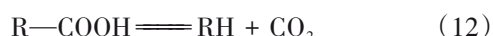
超临界水的强氧化性与黄铁矿的氧化还原反应可形成协同效应,不仅能影响含氧化合物的生成路径和脱羧反应[反应式(12)和反应式(13)]进行程度^[94,95],还可以影响有机质的化学键转化与官能团反应过程。样品CQ油相产物中可检测到酯、酸、醛和醇等多种含氧化合物。其中,羧酸和酯类含量显著低于样品LK(表4),这表明其脱羧反应更为充分。同时样品CQ油相组分中有机硅组分含量高达22.55%,主要为十八甲基环壬硅氧烷和十六甲基七硅氧烷等支链化硅氧烷。这表明,黄铁矿的存在不仅促进了碳链的裂解,还有利于硅氧键的重组和环化反应。在样品LK油相产物中仅检测到酮和醚,未检测到醇类。这一结果表明,超临界水的高温、高压反应环境与黄铁矿反应生成的活性位点,可协同促进羧酸和酯类化合物的脱羧反应,进而释放 CO_2 并生成相应烃类产物。相比之下,样品LK因缺乏黄铁矿这一有效组分,其脱羧反应程度有限,导致

表4 油页岩样品超临界水热解反应油相产物中直链烷烃、酯和酸等组分的相对含量统计

Table 4 Relative contents of *n*-alkanes, esters, carboxylic acids and other components in oil-phase products from SCW pyrolysis of oil shale samples

样品名称	油相组分相对含量/%									
	直链烷烃	酯	酸	烯烃	支链烷烃	醛	环烷烃	酮	醚	醇
LK	78.42	6.20	3.97	3.22	2.24	2.24	1.98	1.24	0.49	0
CQ	61.13	5.93	1.78	0	4.16	2.67	0.59	0	0	1.18

羧酸和酯类化合物含量较多。



红外吸收带的峰面积与油相的物理化学性质密切相关。依据红外光谱峰值的波数位置和峰面积信息,可识别油相组分中不同化学键的类型^[96]。图7为样品LK和样品CQ的热解油相组分的红外光谱数据,波数为2 921 cm⁻¹和2 850 cm⁻¹处为脂肪烃物质的吸收峰,分别对应甲基和亚甲基的C—H对称伸缩振动及非对称伸缩振动区域。波数介于1 330 ~ 1 460 cm⁻¹的区间对应脂肪烃中甲基和亚甲基(其热稳定性低于甲基)的C—H弯曲振动区域。波数为1 605 cm⁻¹处代表芳香环骨架中碳-碳双键(C=C)的伸缩振动特征峰。1 705 cm⁻¹处为酮中羰基(C=O)的伸缩振动区域。波数为1 252 cm⁻¹处为酯基的特征红外吸收峰。

样品LK的油相组分在波数为2 921 cm⁻¹, 2 850 cm⁻¹和1 330 ~ 1 460 cm⁻¹处的吸收峰值相对更高(图7),这一特征表明,在缺乏黄铁矿反应体系促进作用的条件下,有机质裂解过程仅停留在脂肪烷基链的简单断裂阶段,进一步的芳构化反应受到限制;而在芳香环骨架碳-碳双键(C=C)伸缩振动区,样品CQ的吸收峰值明

显高于样品LK,表明黄铁矿的反应体系促进了有机质分子中苯环支链的断裂,形成更多的芳香类化合物,这一结果与组分分析中样品CQ油相产物中芳烃含量较样品LK高4.94%的实验结果相吻合。

上述现象与实验结果分析表明,黄铁矿的氧化还原反应及其原位生成的活性相是促进有机质裂解与芳构化的主要影响因素,原因在于:①促进烷基链的热解断裂反应;②可通过提供酸性环境与铁离子催化位点,促进脂肪链中亚甲基发生脱氢芳构化反应,进而形成稳定的芳香环结构。该反应机制不仅使样品CQ油相产物呈现出更高的芳香类化合物含量和相对较低的脂肪烃含量特征,更能通过强化脱羧反应与官能团重构过程,促进油相产物向轻质化方向转化。

4 结论

1) 方解石的溶蚀作用可影响超临界水热解体系的气体生成平衡。LK油页岩因富含方解石,在超临界水环境中方解石与水发生协同溶蚀作用,释放大量的CO₂,抑制了水-煤气变换反应的正向进行,导致H₂产率降低。而CQ油页岩不含方解石,CO₂生成量较低,对甲烷化反应的抑制作用弱,使得CH₄和H₂产率显著提升。

2) 黄铁矿作为反应物与活性相前驱体,其氧化还原反应及原位生成的磁黄铁矿、磁铁矿和硫等活性相,可有效优化烃类产物结构。超临界水热反应改质过程中,样品CQ中黄铁矿的反应体系可促进重质组分(如沥青质)的裂解,使产物呈现出更强的烷基链裂解与芳构化倾向,芳烃组分生成量增加,进而提升了轻质液态烃产率。而样品LK因缺乏黄铁矿反应体系的促进作用,有机质热解产物以脂肪烃组分为主,且轻质液态烃的产率低于样品CQ。

3) 超临界水体系为油页岩有机质热解转化提供了优良的反应介质。在整个反应体系中,方解石通过溶蚀反应主导CO₂的生成路径,进而抑制H₂生成;黄铁矿则通过释放活性位点,加速有机质分子的断链与重构过程,油相组分中低碳数组分(碳数 ≤ 16)含量明显

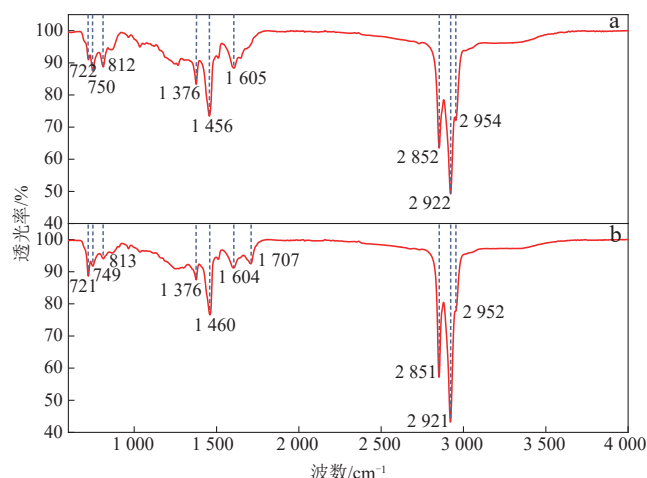


图7 黄县盆地LK(a)与鄂尔多斯盆地CQ(b)油页岩样品超临界水热解反应油相产物的傅里叶变换红外光谱

Fig. 7 FT-IR spectra of oil-phase products from SCW pyrolysis of (a) LK (Huangxian Basin) and (b) CQ (Ordos Basin) oil shale samples

升高,这印证了两类矿物组分对产物演化的差异化影响。

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