The effects of minerals on oil cracking in confined pyrolysis experiments

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Abstract. Confined pyrolysis experiments of oil in the presence and absence of minerals were conducted to reveal the effects of minerals on the oil cracking process. The results indicated that the methane generation rates decreased in the following order: oil alone > oil with clastic minerals > oil with carbonate minerals > oil with clay minerals, and the yields of C\textsubscript{2}-5 decreased in the order: oil with clay minerals > oil with carbonate minerals > oil with clastic minerals > oil alone. That means these minerals inhibited the cracking of C\textsubscript{2}-5 into methane. The inhibiting effect were decreased in the order: clay minerals > carbonate minerals > clastic minerals. Meanwhile, the ratios of i-C\textsubscript{4}/n-C\textsubscript{4} decreased in the order: oil with clay minerals > oil with carbonate minerals > oil with clastic minerals > oil alone. That means the efficiencies of isomerization catalysed by minerals were decreased in the order: clay minerals > carbonate minerals > clastic minerals. Meanwhile, the ratios of C\textsubscript{2}H\textsubscript{6}/C\textsubscript{4}H\textsubscript{6} increased with the order: oil with clay minerals < oil with carbonate minerals < oil with clastic minerals < oil alone. The hydrogenation rates of olefins increased in the following order: clay minerals < carbonate minerals < clastic minerals. The extent of enrichment \textsuperscript{13}C for the generated methane and ethane increased in the order: clastic minerals < carbonate minerals < clay minerals. Such carbon isotopic fractionation during methane and ethane formation was probably induced by the catalytic effect of mineral surface on the terminal methyl group of hydrocarbons. The study of minerals effects on oil cracking may enhance our understanding on the evolution of petroleum reservoirs.

1. Introduction
The clastic minerals, carbonate minerals and clay minerals are three dominated rock-forming minerals of sedimentary rocks [1]. Previous studies have indicated that organic matter (OM) can be closely associated with minerals in geological systems [2-4]. The role of minerals on the pyrolysis of oil has been discussed in many studies [2,3,5-7]. They all demonstrated that the catalytic effects of minerals (especially clay minerals) on the process of oil cracking were ubiquitous [2,3,5-7]. The clay minerals (especially montmorillonite) may promote olefins transfer to alkanes through acidic catalysis and/or hydrogen radical transfer mechanism [5,7,8]. The water which dehydrated from montmorillonite may inhibited the thermal maturation of OM. Meanwhile, this inhibiting effect can be very slight because of the low amount of dehydrated water generated from minerals [5-7]. Additionally, the carbon isotopic
fractionation of gas hydrocarbon can also be induced by the carbonium ion mechanism [9] or mineral surface catalysis on the terminal methyl [7]. However, most of the previous researches focused on the montmorillonite, kaolinite and carbonate minerals [5,8], with little attention to the illite and clastic minerals. This study is to comprehensively investigate the catalytic effects of different rock-forming minerals (including clastic, carbonate and clay minerals) on oil cracking during the confined anhydrous pyrolysis process.

2. Samples and experimental

2.1. Sample
The crude oil was collected from the Ordovician strata (5940–5953 m) of the YM2 well which is located in the Yingmaili Uplift of the Tarim Basin, China. It belongs to the Yingmai 2 Oilfield and mainly reserved in the Lower Ordovician Yijiangfang Formation. This oil reservoir was considered to be of marine origin and mainly derived from Middle-Upper Ordovician successions [10]. The oil reservoir primarily contains oils, with only a few containing gases, the gas oil rate (GOR) was 51 m³/m³ [10,11]. The current temperature of this oil reservoir (115–139 °C; [11]) was too low to crack oil into gases. The bulk compositions of the oil were 54.2% saturates, 19.1% aromatics, 14.9% resins and 13.6% asphaltenes. This oil has a density of 0.89 g/cm³ at 20 °C and sulfur content of 0.66% [11].

2.2. Confined pyrolysis experiments
Six kinds of minerals were used in this study, including calcium carbonate (CaCO₃), magnesium carbonate (MgCO₃), quartz, feldspar, montmorillonite and illite. Those minerals were Soxhlet extracted with a solvent mixture of dichloromethane/methanol (93:7 vol/vol) for 72 h to remove organic contaminations and then dehydrated at 45 °C. Subsequently, the extracted minerals were respectively mixed with the crude oil in different proportion (1:0.2 wt and 1:2 wt) and sealed into gold tubes for further pyrolysis experiments.

All pyrolysis experiments were conducted using sealed gold tubes under a constant confining pressure of 50 MPa with an error of less than 2 MPa. The temperature, measured with an accuracy of ±1 °C by a thermocouple placed within an empty vessel, was first raised from room temperature to 250 °C within 10 h, and then programmed to reach 600 °C at a heating rate of 20 °C/h. After pyrolysis, the gaseous hydrocarbons in the capsules were collected in a special device connected to an Agilent 7890-0322 GC modified by Wasson ECE Instrumentation, as previously described [5,6]. The gas components will be analysed in an automatically controlled procedure. Meanwhile, the remaining gas were taken for hydrocarbon gases isotope ratio mass spectrometry (GC-IRMS) analysis. At least two measurements were performed for each gas sample to confirm the errors were less than ±0.3‰. After the gas compositions and isotope were analysed, the liquid hydrocarbons were ultrasonically extracted using dichloromethane and weighed.

3. Results and discussion

3.1. Yields of gas products
Gas yields from the eleven series of experiments at the heating rate of 20 °C/h are showed in figure 1. The yields of methane increased with temperature in all series. At the highest temperature of 600 °C, the yields of methane ranged from 269.35–403.39 mg/g oil for all series, whereas the yield of oil alone was 393.13 mg/g oil. The methane generation rates for oil with 20% MgCO₃ were significant lower than others especially at the higher temperature (figure 1). That may indicated the magnesium ions at lower content have a stronger inhibitive effect on the methane generation. The methane yields from the eleven series of experiments exhibited only minor differences at temperature < 450 °C. Whereas, at higher temperature stage (> 450 °C), the methane generation rates from cracking of oil in the presence of minerals were slightly lower than oil alone. In addition, the methane yields of the eleven series at the same temperature followed the order: oil with clay minerals < oil with clastic minerals < oil with
carbonate minerals < oil alone. The yields of heavy hydrocarbon gases (C$_2$–5) at first increased to maximum values (318.14–386.43 mg/g oil) at 510 °C and then decreased at higher temperatures (figure 1). The temperatures (ca. 510 °C) for the maximum yield of C$_2$–5 were consistent for the eleven series. At temperature < 510 °C, the yields of C$_2$–5 in the experiments with different minerals showed the same trend to those of methane. Their C$_2$–5 yields followed the order: oil with clay minerals < oil with carbonate minerals < oil with clastic minerals < oil alone. However, when the temperature was > 510 °C, the influence order of different minerals on the yields of C$_2$–5 was reversed to that on the yields of methane. These indicated the cracking rates of heavy hydrocarbons were prohibited by the investigated minerals, and the inhibitive effect decreased in the order: clay minerals > carbonate minerals > clastic minerals. Numerous studies demonstrated that water suppresses organic maturation [5-7] during the thermal evolution process. During pyrolysis, the water generated by the dehydration of clay minerals can react with oil components, resulting in a relatively lower oil cracking rate. However, since it was no doubt that the ratio of dehydrated water/oil is very low in this pyrolysis experiment, the water have only slight effect on the cracking rates of C$_2$–5 [5-7].

The ratios of i-butane/n-butane (i-C$_4$/n-C$_4$) for the eleven series of experiments reached a maximum value at 550 °C, then decreased at higher temperature. The ratios of i-C$_4$/n-C$_4$ were significantly higher in the experiments with clay minerals than other series (figure 1). It was consistent with previous studies [5,7], and can be contributed to the different pH values and acidic sites between clay mineral surfaces and other minerals [5,7]. Namely, the lower pH values of minerals or more acidic sites on its surfaces, the higher branched iso-alkanes yields. Thus, the isomerization catalyzed by minerals were decreased in the order: clay minerals > carbonate minerals > clastic minerals. Gas olefins are unstable and readily hydrogenated into saturated hydrocarbons [8]. Thus, the ratios of ethene/ethane (C$_2$H$_4$/C$_2$H$_6$) were decreased with increasing temperature (figure 1). The low ratios of C$_2$H$_4$/C$_2$H$_6$ indicated the high hydrogenation rate of olefins. Thus, the ratios of C$_3$H$_6$/C$_2$H$_6$ demonstrated that the hydrogenation rate of olefins catalyzed by minerals increased with the order: clay minerals < carbonate minerals < clastic minerals. Pan et al. 2010 [7] suggested such phenomenon was related to the transfer mechanism for the
hydrogen radical. Clay minerals may inhibit the transfer of hydrogen radicals from liquid oil components to olefins, resulting in a higher olefins/alkanes ratio.

3.2. Stable carbon isotopic compositions of generated gas
Carbon isotope compositions of methane (δ¹³C₁), ethane (δ¹³C₂) and carbon dioxide (δ¹³CΟ₂) generated from eleven pyrolysis experiments are compared in figure 2. The δ¹³C values of methane and ethane at first become more negative and then become less negative with increasing temperature for all series of experiments. This phenomenon was observed in many previous researches [12,13]. They suggested that it could be two or more precursors with different isotope compositions for the generated gas. The yield of total gas hydrocarbons produced in the low temperature stage (< 456 °C) are too low. Thus, the differences in δ¹³C values of methane and ethane between eleven series are larger than at higher temperatures. Figure 2 revealed that the carbon isotopes of methane and ethane were lighter when the minerals presence than oil alone in the high temperature stage (> 456 °C). That means the carbon isotopes of methane and ethane become enriched in ¹²C when the minerals were existed. The extent of enrichment ¹³C for the generated methane and ethane increased in the order: clastic minerals < carbonate minerals < clay minerals.

The δ¹³C values of CO₂ for oil alone, oil with clay and clastic minerals, ranged from -35.00‰ to -30.00‰. In addition, the δ¹³C values of CO₂ decreased in the order: oil > oil with clastic minerals > oil with clay minerals, the same as the carbon isotopes of methane and ethane. Whereas, the δ¹³C values of CO₂ for oil with carbonate minerals were heavier than other series. The δ¹³C values of CO₂ for oil with CaCO₃ and MgCO₃, ranged from -25.00‰ to -20.00‰ and from -20.00‰ to -15.00‰, respectively. The variation of δ¹³C values of CO₂ between the series of oil with carbonate minerals and oil with clay minerals were around 10‰. The effect of both minerals on carbon isotopic fractionation during methane and ethane formation appears to be induced by mineral surface catalysis on the terminal methyl group of hydrocarbons [7]. Whereas, the variation of δ¹³C values of CO₂ between carbonates and other minerals was probably because the carbonium ion reaction will happen when the former were existed [7].

![Figure 2](image-url)

Figure 2. The δ¹³C values of methane, ethane and carbon dioxide generated by oil cracking experiments at various temperatures.
3.3. Amounts of bitumen and liquid hydrocarbons

For the series of mineral catalytic pyrolysis experiments, bitumens produced in all the eleven experiments increased from 34.97–240.98 mg/g oil at 384 °C to the highest 414.70–560.67 mg/g oil at 600 °C (figure 3). The amounts of liquid hydrocarbons produced during pyrolysis for all the series decreases substantially from 700.00–897.81 mg/g oil at 384 °C to the highest 44.84–90.09 mg/g oil at 600 °C. The liquid hydrocarbon yields of the eleven series at the same temperature followed the order: oil with clay minerals > oil with clastic minerals > oil with carbonate minerals, and these differences between series decreased with the temperature increasing. This indicated the inhibitive effect on oil cracking between minerals were decreased in the order: clay minerals > clastic minerals > carbonate minerals. The trend of generation ratios of bitumen with different minerals showed no systematic variations (figure 3).

![Figure 3](image)

Figure 3. The amounts of extracted liquid hydrocarbons and bitumen produced during pyrolysis experiments at various temperatures.

4. Conclusion

The effects of minerals (i.e., CaCO₃, MgCO₃, quartz, feldspar, montmorillonite and illite) on the cracking oil were demonstrated through pyrolysis experiment in a confined system (gold capsules). The following conclusions can be made:

1. The inhibitive effect for the cracking of C₂⁻₅ into methane between different minerals were decreased in the order: clay minerals > carbonate minerals > clastic minerals.
2. The isomerization catalyzed by minerals were decreased in the order: clay minerals > carbonate minerals > clastic minerals. Meanwhile, the hydrogenation rates of olefins which influenced by the hydrogen radical transfer mechanism from minerals, were increased with the order: clay minerals < carbonate minerals < clastic minerals.
3. The extent to promote methane and ethane to enriched ¹²C increased in the order: clastic minerals < carbonate minerals < clay minerals. These carbon isotopic fractionation during methane and ethane formation appeared to be induced by mineral surface catalysis on the terminal methyl group of hydrocarbons. Whereas, influenced by the carbonium ion reaction mechanism from carbonate minerals, the δ¹³C values of CO₂ for oil plus carbonates showed heavier carbon isotopic values than other series.

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