

Research Advances

The Enormous Potential of Gas Generation from Carboxylic Acid Salts

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Objective

Up to 45% of total organic carbon (TOC) was probably lost during acid treatment in carbonate-rich rocks (Froelich, 1980). Some scientists thought these acid-soluble organic matters were largely contributed from carboxylic acid salts, which were commonly developed in alkaline carbonate formations and could potentially be excellent sources for natural gas stored in Early Paleozoic carbonate rocks in the Ordos Basin (Chong and McKay, 1984; Liu et al., 2017). However, the gas generation from carboxylic acid salts was not systemically studied. As reported in Liu et al. (2013), these carboxylic acid salts were dominated by calcium stearate and calcium palmitate. Thus, gold-tube closed pyrolysis using calcium stearate as reactant was conducted to investigate the gas potential of carboxylic acid salts.

Methods

The model compound calcium stearate was loaded into gold tubes, which were then sealed by argon arc welding. Then the gold tubes were heated from room to target temperatures at a heating rate of 2°C/h. The gas products were released into an auxiliary and closed glass tube and measured by Agilent 6890 GC. The detailed procedure to quantify the gaseous products can be found in Wang et al. (2008). The solid products were analyzed using the Praying Mantis™ diffuse reflection accessory (Harrick Scientific Products INC) for a Bruker Vertex-70 Fourier transform infrared spectrometer. The inorganic (carbonate) $\delta^{13}\text{C}$ values were obtained by a Thermo Finnigan Gas Bench II-MAT 253 plus mass spectrometry in Northwest University, Xi'an, China.

Results

The methane yield did not increase rapidly until 394°C in calcium stearate series (Fig. 1a). The maximum C_1 yield was achieved at 600°C (594.5 mg/gTOC). This value indicated approximately half of TOC of calcium stearate (594.5/1000*12/16*100%) converted into gaseous hydrocarbon at the maximum pyrolysis temperature. The

methane production from kukersite kerogen (marine and type I organic matter) started at much lower temperature (360°C) and obtained the peak yield of 304.3 mg/gTOC at 600°C (Wang et al., 2013). This value implied that the maximum conversion of TOC of kukersite kerogen was approximately 23% (304.3/1000*12/16*100%). In contrast, the conversion ratio of organic carbon into gaseous hydrocarbon in calcium stearate was about twice as much as that of type I kerogen.

The infrared spectrum of original calcium stearate was labeled as “untreated” (Fig. 1b). The peaks at 2926 cm^{-1} and 2850 cm^{-1} were attributed to the CH_2 asymmetrical and symmetrical stretching vibration, whilst the peaks at 1583 cm^{-1} , 1546 cm^{-1} and 1430 cm^{-1} were ascribed to COO -asymmetrical and symmetrical stretching vibration coupled with Ca^{2+} ion, respectively. At 394°C, peaks around 1546 cm^{-1} and 1430 cm^{-1} began to disappear, indicating the decomposition of calcium stearate. At 538°C, peaks at 2926 cm^{-1} , 2850 cm^{-1} , 1583 cm^{-1} , 1546 cm^{-1} and 1430 cm^{-1} could not be seen any more. Instead, the peaks at 1452 cm^{-1} (C-O asymmetrical stretching vibration of calcite), 875 cm^{-1} (C-O out-of-plane bending vibration of calcite) and 711 cm^{-1} (C-O in-plane bending vibration of calcite) became obvious. These results illustrated that the decomposition of calcium stearate led to the formation of calcite as the increasing pyrolysis temperature. The inorganic $\delta^{13}\text{C}$ of carbonate generated at 538°C was -24.9‰ , implying its organic origin. In other word, the conversion of organic carbon into inorganic carbon occurred during the pyrolysis of calcium stearate, which could be used to identify the process of hydrocarbon generation from carboxylic acid salts. It worth noticed that the negative $\delta^{13}\text{C}$ of carbonate was not an exclusive proxy indicating the decompositions of carboxylic acid salts. Other geological process such as thermochemical sulfate reduction (TSR) could also result in very negative $\delta^{13}\text{C}$ of carbonate.

Conclusions

The maximum yield of methane (594.5 mg/gTOC) generated from calcium stearate was approximately twice as much as that of type I kerogen (304.3 mg/gTOC). This result indicated carboxylic acid salts were even more

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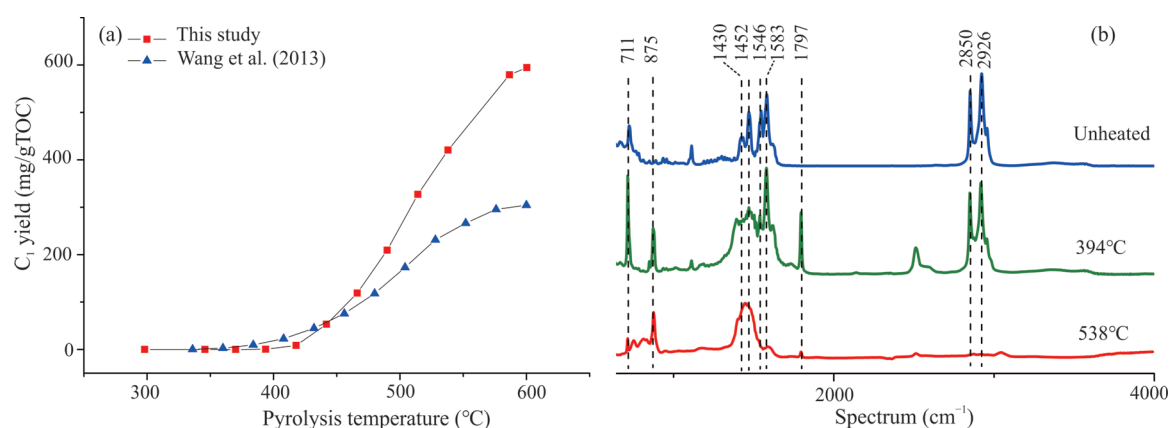


Fig. 1 (a) Comparison of methane yields generated from calcium stearate (this study) and kukersite kerogen (Wang et al., 2013), respectively; (b) the diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) results of the solid products.

effective gas source than conventional kerogen. Carboxylic acid salts were lost during the acid treatment in carbonate-rich rocks and were not involved in the TOC of carbonate-free source rocks. As potential and ignored gas sources for natural gas, carboxylic acid salts might account for the self-generation and self-accumulation natural gas in over mature Paleozoic carbonate rocks in Ordos Basin.

It is important to identify the hydrocarbons generated from carboxylic acid salts rather than from kerogen or oil. The calcite with very negative $\delta^{13}\text{C}$ could be a proxy to indicate the hydrocarbon generation from carboxylic acid salts, when the TSR-origin calcite could be ruled out.

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