Thermochemical reduction of magnesium sulfate by natural gas: Insights from an experimental study

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(Received January 12, 2010; Accepted August 2, 2010)

Thermochemical reduction of MgSO4 by natural gas was carried out in the presence of water. Chemical and carbon isotopic variations were characterized with microcoulometry, gas chromatography, FT-IR, XRD and GC-C-IRMS. It was found that natural gas reacted with MgSO4 to produce H2S, CO2, MgO and solid bitumen as the main products of thermochemical sulfate reduction (TSR). Gas dryness, gas souring index and the extent of reaction parameter positively correlated with temperature. The extent of acidulation and oxidation of natural gas were intensified as TSR proceeded. TSR has induced an evident carbon isotope fractionation in natural gas. Based on the experimental results, the reaction mechanism was tentatively investigated. It was found that the catalytic role of a metallic ion in the TSR process may be controlled by at least three factors: the charges and the radius of a metallic ion and the number of Lewis acid centers scattered on the surface of the sulfates. The last factor is largely determined by the amount of water in a TSR system. A small amount of water and metallic ions with more charges and short radius may effectively initiate the TSR.

Keywords: MgSO4, natural gas, thermochemical sulfate reduction (TSR), carbon isotope fractionation, reaction mechanism

INTRODUCTION

The increasing demand for oil and natural gas has made H2S-bearing gas an important choice for China’s energy supply. H2S is generally an undesirable component of natural gas. Where present, H2S not only can critically affect the economic proportion of hydrocarbon gas, but is highly toxic to lives and corrosive for production equipment. H2S-rich gases (>10% H2S) are generally attributed to thermochemical sulfate reduction (TSR), an oxidation-reduction reaction between hydrocarbons and sulfates in deep carbonate reservoirs, which has been well-documented due to the critical role it plays in the formation of H2S-bearing gas (e.g., Krouse et al., 1988; Machel et al., 1995; Machel, 2001; Worden and Smalley, 1996; Worden et al., 1995, 1996, 2000; Cai et al., 2003, 2004; Li et al., 2005; Zhang et al., 2005).

Many experimental works have been carried out to study the reaction kinetics and mechanisms of TSR (Toland, 1960; Dhannoun and Fyfe, 1972; Trudinger et al., 1985; Kiyosu, 1980; Kiyosu and Krouse, 1990, 1993; Goldhaber and Orr, 1995; Cross et al., 2004; Pan et al., 2006; Yue et al., 2005, 2006; Ding et al., 2007, 2008a, 2008b, 2008c, 2010a, 2010b; Zhang, S. C. et al., 2008; Zhang, T. W. et al., 2007, 2008; Ma et al., 2008; Amrani et al., 2008). Especially, Pan et al. (2006) have conducted simulation experiments between gaseous hydrocarbons and sulfates in which gaseous hydrocarbons were prepared by kerogen pyrolysis. It should be noted that all their gaseous pyrolysates samples contained various contents of H2S, used as an initiator in the other experiments (Goldhaber and Orr, 1995). The amount of H2S in the selected nine small capsules ranges from 0.01 mmol/g TOC to 0.67 mmol/g TOC. Compared with the previous work of Pan et al. (2006), all thermal simulations in this paper are carried out using natural gas samples free of sulfur species. As MgSO4 is the only sulfur source initially present in the present experiments, any hydrogen sulfide formed must arise from TSR. The objectives of this study are:

1) To determine the chemical and carbon isotopic variations of natural gas in the process of TSR;
2) To investigate the reaction mechanism between natural gas and MgSO4 and discuss the catalysis of metallic ions in the process of TSR.

The results may further improve our understanding of thermochemical origin of H2S in natural gas.

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EXPERIMENTAL

All thermal simulation experiments were carried out using an autoclave of 200 ml at high temperature and high pressure. The sample basket is a quartz glass cylinder with a height of 80 mm and diameter of 10 mm. The quartz glass cylinder has a bottom to hold MgSO₄ powder and its other side is left open. The basket was placed on the bottom of the reactor. Each runtime, the basket with about 2 g of MgSO₄ powder was put into the reactor, and then the reactor was vacuumed. About 10 ml of distilled water was aspirated into the autoclave through an inlet point, and then the autoclave was charged with natural gas sample to a given pressure. The natural gas sample was obtained from a natural gas well in Langfang (Hebei province, China) and its composition was shown in Table 1. The reactor was heated to 450 °C, 480 °C, 510 °C and 540 °C directly and the heating time was of 168 h. The oven temperature was programmed at 50 °C, 480 °C, 510 °C, 540 °C and 550 °C for 3 h, respectively.

Table 1. Chemical composition of the gaseous products at different temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₂H₄</th>
<th>C₃H₈</th>
<th>C₃H₆</th>
<th>n-C₄H₁₀</th>
<th>i-C₄H₁₀</th>
<th>n-C₅H₁₂</th>
<th>i-C₅H₁₂</th>
<th>H₂</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>78.560</td>
<td>11.847</td>
<td>BD</td>
<td>4.323</td>
<td>BD</td>
<td>1.038</td>
<td>0.715</td>
<td>0.257</td>
<td>0.281</td>
<td>0.107</td>
<td>BD</td>
<td>2.872</td>
<td>BD</td>
</tr>
<tr>
<td>450</td>
<td>86.436</td>
<td>8.633</td>
<td>0.007</td>
<td>1.029</td>
<td>0.054</td>
<td>0.005</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>0.197</td>
<td>3.432</td>
<td>0.188</td>
</tr>
<tr>
<td>480</td>
<td>88.542</td>
<td>5.609</td>
<td>0.055</td>
<td>1.145</td>
<td>0.141</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>1.212</td>
<td>3.989</td>
<td>0.253</td>
</tr>
<tr>
<td>510</td>
<td>89.820</td>
<td>3.354</td>
<td>0.095</td>
<td>0.009</td>
<td>0.187</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>1.520</td>
<td>4.439</td>
<td>0.432</td>
</tr>
<tr>
<td>540</td>
<td>90.016</td>
<td>1.502</td>
<td>0.141</td>
<td>0.001</td>
<td>0.202</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>1.793</td>
<td>5.033</td>
<td>1.027</td>
</tr>
<tr>
<td>570</td>
<td>90.313</td>
<td>0.130</td>
<td>0.181</td>
<td>BD</td>
<td>0.212</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>2.085</td>
<td>5.146</td>
<td>1.178</td>
</tr>
</tbody>
</table>

The gas composition at 25°C is the original composition of natural gas. BD: below detection level.

The properties of the products were characterized by microcalorimetry, gas chromatography, FT-IR, XRD and GC-C-IRMS methods, respectively. The microcalorimetry with a model of WK-2B (Jiangsu, China) was used to determine total sulfur of gaseous products which were injected into the microcalorimeter and combusted with oxygen in the air. Then hydrogen sulfur was converted into SO₂, which was carried by nitrogen flow to react with iodine in a titration cell of the microcoulometer. The consumed iodine would be supplemented by electric cracking of KI in the cell. According to Faraday’s law, the content of H₂S in natural gas could be calculated with the electric quantity consumed in the process of electric cracking.

Analysis conditions were as follows: the furnace entrance temperature was 500 °C and exit temperature was 850 °C. The temperature of gasification zone was 500 °C. The flow rates of air, nitrogen, and sample gas were 40 mL/min, 160 mL/min, and 30 mL/min, respectively.

Characterization

The products of the calcinations were analyzed using a microcoulometer and a gas chromatograph, equipped with a thermal-conductivity detector, a flame-ionization detector, a model of WK-2B (Jiangsu, China) and a Nicolet 750 FT-IR spectrometer. The gas composition at 25°C is the original composition of natural gas.

Composition of gaseous reaction products was determined with a microcoulometer (WK-2B, Jiangsu, China) and a Nicolet 750 FT-IR spectrometer. The properties of the products were characterized by microcalorimetry, gas chromatography, FT-IR, XRD and GC-C-IRMS methods, respectively. The microcalorimetry with a model of WK-2B (Jiangsu, China) was used to determine total sulfur of gaseous products which were injected into the microcalorimeter and combusted with oxygen in the air. Then hydrogen sulfur was converted into SO₂, which was carried by nitrogen flow to react with iodine in a titration cell of the microcoulometer. The consumed iodine would be supplemented by electric cracking of KI in the cell. According to Faraday’s law, the content of H₂S in natural gas could be calculated with the electric quantity consumed in the process of electric cracking.
 ware OMNIC v. 7.0, by averaging 32 scans at a spectral resolution of 4 cm$^{-1}$ under dried nitrogen flow (10 cm$^3$/min) conditions. All spectra were smoothed using the “automatic smooth” function of the above software, which uses the Savitsky-Golay algorithm (95-point moving second-degree polynomial). After that, the baseline was corrected using the “automatic baseline correct” and the spectra scale was normalized with the “normalize scale” function. The spectroscopic region 4000 cm$^{-1}$ to 400 cm$^{-1}$ was used for hierarchical cluster analysis. The characteristics of the crystalline structure of the solid products were determined using powder XRD. After calcination, the products were mechanically crushed and sieved to size of <200 mesh. X-ray diffraction was carried out at room temperature with a RIGAKU D/max-rB automatic X-ray diffractometer (Rigaku Co., Tokyo, Japan). About 30 mg powdered solid products were kept in a quartz block and pressed onto the quartz block using a glass slide to obtain a uniform distribution. The 2$\theta$ Bragg angles were scanned over a range of 15°–85° at a scanning speed of 2°/min with a 0.02° angular resolution, using graphite monochromated Cu–K$_\alpha$ radiation source ($\lambda$ = 0.154056 nm, germanium monochromator) and a nickel filter. The tube current was 150 mA and the tube voltage was 50 kV. The experiment parameters were as follows: DS = 1°, SS = 1°, RS = 0.3 mm. The database of the Joint Committee on powder diffraction data was used for the interpretation of XRD spectra.

Stable isotope analysis of $^{13}$C/$^{12}$C in gas samples was performed using a gas chromatograph combustion isotope ratio mass spectrometer GC–C–IRMS Finnigan (Thermoquest, Bremen, Germany). The HP 6890 GC was fitted with a Pora Plot Q column (30 m × 0.32 mm i.d., 10 µm film thickness; Chrompack, Germany) and helium was used (99.996% purity; 2.6 ml·min$^{-1}$) as carrier gas. The column head pressure was 7.5 psi. The GC oven temperature was initially held at 45°C for 3 min, ramped from 45 to 200°C at 15°C/min, and held at 200°C for 5 min. Carbon isotope ratio calculations were performed using CO$_2$ as a reference gas. Reported isotopic data represented the arithmetic means of at least two repeated analyses, and all carbon isotopic values were reported in per mil (‰) relative to the PDB standard. The working standards were CO$_2$ (99.998% purity) inter-calibrated against NBS22 and expressed in the delta notation versus PDB carbonate:

$$
\delta^{13}C = 10^{3}\left(\frac{R_{sa}}{R_{st}} - 1\right).
$$

Where $R = ^{13}C/^{12}C$ of sample (sa) and standard (st), respectively. The $\delta^{13}C$ of NBS22 relative to PDB is −29.4‰ (Zheng and Chen, 2000). The analysis of $\delta^{13}C$ for the gas product was carried out at the Research Institute of Petroleum Exploration and Development–Langfang Branch, PetroChina Ltd, China (courtesy of Li, Z. S.).

RESULTS AND DISCUSSION

Analysis of the solid products

It has been reported that TSR forms a series of organic compounds, some of which polymerize and precipitate as solid bitumen (Machel, 2001). In the present work, some black material was observed in the solid products. After calcinations at 500°C in the muffle, the black material became white. Therefore, the black deposit probably corresponded to be solid bitumen. FT-IR spectrum
of solid products after calcination at the temperature of 510°C is shown in Fig. 1. In Fig. 1, the peaks at 3416 cm$^{-1}$ and 1643 cm$^{-1}$ are the vibrational band of water. The peak at 1176 cm$^{-1}$ is the vibrational band of sulfate radical. Especially, the appearance of peak at 461 cm$^{-1}$ can be explained by the formation of MgO (Peng and Liu, 1982). X-ray powder diffraction patterns of solid reaction products at 510°C (after calcination) are shown in Fig. 2. From the patterns, two distinct crystallographic phases, MgO and MgSO$_4$ are found to coexist in the products. These results suggest that MgO is produced during TSR process, which coincides with the results of FT-IR.

Analysis of the gaseous products

Chemical composition of the gaseous reaction products is listed in Table 1. The original composition of natural gas is CH$_4$, C$_2$H$_6$, C$_3$H$_8$, C$_4$H$_{10}$, and CO$_2$ besides a little of C$_5$H$_{12}$ and C$_6$H$_{14}$ (Table 1). With the increasing temperature, C$_2$–C$_6$ hydrocarbons disappear first of all, and the amounts of C$_2$H$_6$ and C$_3$H$_8$ are decreasing gradually. The ratio of CH$_4$ in the gas composition increases as other hydrocarbons decrease or disappear. It is obvious in Table 1 that the content of H$_2$S increases as temperature grows, which indicates that high temperatures are favorable for the production of H$_2$S. Although the origi-
creasing temperature, the ratio of CH4 in the gas composition (3 MPa) and 10 ml of distilled water. With the increase of the hydrocarbon gas population (Worden and Smalley, 1995). The ratio CO2/(CO2+H2S) is used to monitor the changing amounts of H2S and hydrocarbons in natural gas (Worden et al., 1988). Relative relationships were observed between the content of alkenes, H2 and CO with increasing temperature as outlined in Fig. 4. The successive increase of ethylene and propylene were possibly derived from the oxidation of natural gas by MgSO4, the thermal cracking of natural gas or even the secondary reaction between solid bitumen, hydrogen and water under high temperatures. H2 was mainly from the decomposition of natural gas. CO might be the intermediate of TSR or from the reduction of part of CO2 by H2. The above analysis of the reaction products leads to the inference that the oxidation of natural gas by MgSO4 had occurred. H2S, CO2, MgO and solid bitumen are the main products of the reaction between natural gas and MgSO4.

At the experimental temperatures between 450°C and 570°C, the carbon isotopic ratio of methane shifts continuously from −39.5‰ to −38.0‰, and δ13C values of ethane increased from a starting value of −24.0‰ to −20.1‰ in the most reacted sample (Table 2, Fig. 5). The greater carbon isotope fractionation of ethane than methane during experiments implies that ethane was depleted to a greater degree during TSR. Similarly, it could be reasonably deduced from Table 2 that variations of δ13C values of CH4 should also have the same increasing trend as those of methane and ethane despite unavailable data from 510°C to 570°C. In contrast with δ13C values of methane and ethane, δ13C values of CO2 become more negative during the process of TSR. Carbon in the last stages is the original composition of natural gas.

**Table 2. Carbon isotopic composition of the gaseous products at different temperatures**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>δ13C(CH4)</th>
<th>δ13C(H2)</th>
<th>δ13C(CH4)</th>
<th>δ13C(CO2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>−40.4</td>
<td>−27.5</td>
<td>−24.5</td>
<td>−15.5</td>
</tr>
<tr>
<td>450</td>
<td>−39.5</td>
<td>−24.0</td>
<td>−23.1</td>
<td>−22.5</td>
</tr>
<tr>
<td>480</td>
<td>−39.4</td>
<td>−23.6</td>
<td>−19.8</td>
<td>−24.0</td>
</tr>
<tr>
<td>510</td>
<td>−38.5</td>
<td>−23.0</td>
<td>BD</td>
<td>−25.1</td>
</tr>
<tr>
<td>540</td>
<td>−38.3</td>
<td>−20.7</td>
<td>BD</td>
<td>−31.4</td>
</tr>
<tr>
<td>570</td>
<td>−38.0</td>
<td>−20.1</td>
<td>BD</td>
<td>−31.9</td>
</tr>
</tbody>
</table>

The gas composition at 25°C is the original composition of natural gas.
BD: below detection level.
increasing temperature.

MgSO₄ may consist of some elementary steps as follows:

\[
6C_nH_{2n+2} + (4n+2)\text{MgSO}_4 \rightarrow (4n+2)\text{MgO} + (5n+1)\text{CO}_2 + (4n+2)\text{H}_2\text{S} + (2n+4)\text{H}_2\text{O} + (n-1)\text{C}. \quad (2)
\]

Where, \( n = 1, 2, 3 \ldots \).

The reaction of natural gas-MgSO₄ may consist of some elementary steps as follows:

\[
\text{MgSO}_4 \rightarrow \text{Mg}^{2+} + \text{SO}_4^{2-} \quad (3)
\]

\[
6\text{C}_n\text{H}_{2n+2} + (4n+2)\text{SO}_4^{2-} \rightarrow (4n+2)\text{CO}_2^{2-} + (n-1)\text{CO}_2 + (4n+2)\text{H}_2\text{S} + (2n+4)\text{H}_2\text{O} + (n-1)\text{C} \quad (4)
\]

\[
\text{Mg}^{2+} + \text{CO}_2^{2-} \rightarrow [\text{MgCO}_3] \rightarrow \text{MgO} + \text{CO}_2. \quad (5)
\]

When water is vaporized under high temperatures and then adheres to the surface of magnesium sulfate, the ionic bond of Mg²⁺-SO₄²⁻ can easily be broken and the reactive SO₄²⁻ is given out as is shown in Eq. (3). Because the chemical structure of SO₄²⁻ is most stable, Eq. (4) may be a rate-controlled step of the whole process of TSR. Mg²⁺ from the dissolved magnesium sulfate can be united with CO₃²⁻ produced in Eq. (4), which leads to the formation of MgCO₃. MgCO₃ is thermodynamically unstable under high temperatures. In fact, MgCO₃ begins to decompose and produce MgO and CO₂ at 402°C (Dean, 1991). So Eq. (5) may be a very fast process at the range of simulation temperatures (450–570°C). Although the rate of reaction of natural gas-SO₄²⁻ is slow as discussed above, once few of CO₃²⁻ is generated from TSR system, it will be quickly transformed to CO₂ according to Eq. (5).

In the reaction system, by inductive effect, Mg²⁺ generates electrostatic fields which may affect/change the distribution of charges of natural gas molecular, and dynamically polarize C–H bonds and C–C bonds to make them more easily break. The amount of water (10 ml) used in the experiments is small compared with the volume of the reactor (200 ml). In other words, the volume of water accounts for only 5% of the volume of the reactor. When temperature exceeds 100°C, the small amount of liquid water is vaporized and converted into gaseous water. At this time, from the viewpoint of physical chemistry, water is at an unsaturated state. According to the study of Tanabe (1970), unsaturated water can maximize the number of Lewis acid centers scattered on the surface of magnesium sulfate and strengthen the surface acidity of sulfates. Thus, a small amount of water in the reaction system can effectively enhance the oxidation of MgSO₄. In a TSR zone, potential catalysis of metallic ions is believed to be closely associated with the amount of water. Zhang, T. W. et al. (2008) found that the smaller the mole ratio of H₂O/MgSO₄, the easier the oxidation of hydrocarbons by a sulfate, which is in accordance with our present investigation.

In the previous simulation experiments, sulfur (Cross et al., 2004; Amrani et al., 2008), hydrogen sulfide (Kiyosu and Krouse, 1990, 1993; Amrani et al., 2008) or some organic sulfides (Amrani et al., 2008) were added to the reaction systems to initiate TSR. Otherwise, Na₂SO₄, Na₂SO₃ or CaSO₄ hardly reacts with hydrocarbons free of sulfur (Yue et al., 2005, 2006; Ding et al., 2007, 2008c, 2010b). The monovalent metallic ions such as K⁺ and Na⁺ can also to some extent generate electrostatic fields by inductive effect. However, the charges of K⁺ and Na⁺ are less than those of Mg²⁺, and the radius of K⁺ and Na⁺ is longer than that of Mg²⁺. The magnitude of
electrostatic fields generated from K\(^+\) or Na\(^+\) is too weak to dynamically polarize C–H or C–C bonds of hydrocarbons, and hardly make them break. Ca\(^{2+}\) has the same charges as Mg\(^{2+}\). Compared with MgSO\(_4\), besides most stable chemical structure and the low solubility, the low reactivity of CaSO\(_4\) should also be attributed to the longer radius of Ca\(^{2+}\) than that of Mg\(^{2+}\). The longer radius of Ca\(^{2+}\) weakens the magnitude of the electrostatic fields from Ca\(^{2+}\). Thus, the electrostatic fields generated by inductive effect of Ca\(^{2+}\) hardly polarize C–H or C–C bonds of hydrocarbons, and then make them inactively involved in TSR.

Based on the above discussion, it can be deduced that the catalytic role of a metallic ion in TSR process is controlled by at least three factors: the charges of a metallic ion, the radius of a metallic ion, and the number of Lewis acid centers scattered on the surface of the sulfates. The first two factors are associated with the nature of a metallic ion. The last factor is largely determined by the amount of water in a TSR system. A small amount of water and metallic ions with more charges and short radius may effectively initiate TSR. Some sulfates such as Al\(_2\)(SO\(_4\))\(_3\) and Fe\(_2\)(SO\(_4\))\(_3\) should be more active than MgSO\(_4\), because Al\(^{3+}\) and Fe\(^{3+}\) have more charges and shorter radius than those of Mg\(^{2+}\). This presumption needs further evidence and proof from theoretical analysis and simulation experiments (Ding et al., 2008c).

**Geochemical implications**

Under the appropriate geochemical conditions, TSR represents a mechanism for the destruction of hydrocarbons and the production of H\(_2\)S-rich natural gas. It has been suggested that TSR occurs at the gas-water transition zone (Worden et al., 2000). The reactive sulfate for TSR is dissolved sulfate (SO\(_4^{2-}\)) that is mainly derived from dissolution of solid calcium sulfate (primarily gypsum: CaSO\(_4\) [2H\(_2\)O]) and anhydrite: CaSO\(_4\)) (Machel, 2001). Although anhydrite appears to be the reactive oxidant and is replaced by calcite and dolomite in natural TSR reservoirs (Machel, 2001), it is generally not used in laboratory TSR studies due to its low solubility (Toland, 1960; Kiyosu and Krouse, 1993; Goldhaber and Orr, 1995; Cross et al., 2004). In the present study, it was found that in the presence of a small amount of water, natural gas can react with MgSO\(_4\) to produce H\(_2\)S at least up to 450°C. The threshold temperature (450°C) for initiating TSR is lower than our previous studies (490°C) using solid calcium sulfate (Ding et al., 2007). Furthermore, the content of oxidized hydrocarbons at 450–570°C increases substantially, which is attributed to the presence of Mg\(^{2+}\) and water in TSR system. This provides compelling experimental evidence that the stability of natural gas at elevated temperatures in natural environments is not a simple function of time and temperature alone (Machel, 2001).

For the marine sedimentary system dominated by types I and II kerogens, the catalysis of metallic ions has a strong effect on the stability of natural gas as well as on the formation of high H\(_2\)S in natural gas. Especially for some metallic ions that initiate TSR, such as Mg\(^{2+}\), they are believed to play a key role in the formation of high H\(_2\)S gas. According to our study, Mg\(^{2+}\) is recognized as an important reaction catalyst that plays an integral role in regulating the direction, rate, and the extent of TSR process. Mg\(^{2+}\) is common and widespread in deep burial diagenetic settings. It is well known that dolomite and magnesite are the two main carbonate minerals after which the diagentic carbonates formed. These carbonate minerals are always associated with calcium sulfate in the precursor deposits. In the presence of excess water, dolomite and magnesite can release Mg\(^{2+}\), and the dissolution of interbedded gypsum gives out reactive SO\(_4^{2-}\). On the other hand, the common occurrence of Mg\(^{2+}\)–SO\(_4^{2-}\) ion pairs can also seen in dedolomitization processes and the accompanying formation of epsomite (MgSO\(_4\)·7H\(_2\)O) efflorescences as a by-product in the evaporate sequences, which has been widely documented (Jacobs et al., 1982; Budai et al., 1984; Sánchez-Moral et al., 1993; Cañaveras et al., 1996). The calcitization of magnesite can also release dissolved magnesium ion and sulfate ion (Cañaveras et al., 1998). So, Mg\(^{2+}\) and SO\(_4^{2-}\) should be always present in the deep carbonate reservoirs.

However, it should be noted that there are innumerable examples of sweet sulfate-bearing sandstone and limestone natural gas accumulations (Cross et al., 2004). The continuing co-existence of sulfate minerals and natural gas in many reservoirs filled millions of years ago, cannot be only controlled by temperature and metallic ions. This apparent contradiction is reinforced by further experimental evidence which suggest that TSR is simultaneously controlled by the amount of water in a TSR system. Fluid inclusion and isotopic evidence (Worden and Smalley, 1996) suggest strongly that water is an essential medium for TSR. According to our previous simulation experiments (Yue et al., 2005, 2006; Ding et al., 2007, 2008a, 2008b, 2008c, 2010a) and the present study, it is found that under anhydrous conditions or in the presence of excess water, the reactions between hydrocarbons and sulfates hardly occur in comparison with TSR systems containing only a small amount of water. Under anhydrous conditions, the bond of Mg\(^{2+}\)–SO\(_4^{2-}\) is hardly ruptured to release reactive SO\(_4^{2-}\). On the other hand, the excess of water undoubtedly dilutes the concentrations of metallic ions in the gas reservoirs and thus weakens their catalysis during TSR. According to Tanabe (1970), under anhydrous conditions in the presence of excess water, the surface acidity of sulfates is so small that the oxidation of sulfates can be absolutely omitted, which may
account for low reactivities of sulfates under the above conditions. So, in a TSR zone metallic ions (Machel, 2001) and water (Worden and Smalley, 1996) are two important factors for the initiation of TSR, especially potential catalysis of metallic ions are closely associated with the amount of water. Incorporation of such factors into geochemical models will further improve prediction of the occurrence of H2S in natural environments over geologic time.

Comparison of the experimental results with other work

In TSR systems, branched and n-alkanes in the gasoline range appear to be the most reactive, followed by cyclic and mono-aromatic species in the gasoline range, as shown by isotopic and/or gas-chromatic data (Krouse et al., 1988; Manzano and Rooney, 1996; Zhang et al., 1997). Methane is the most stable of all possible reactive organic compounds (e.g., Orr, 1990) and would be the last one to go, not the first or the only one, as has been asserted in some studies (Heydari and Moore, 1989; Worden et al., 1996). There are few field case studies where methane has been conclusively demonstrated to be the only or even the major organic reactant (Machel, 1998). A dry natural gas sample was used in the present study of TSR process. If the starting gas is wet, then the chief reacting compounds have higher carbon numbers, the composition of reaction products varies accordingly (Ding et al., 2008a, c; Zhang, T. W. et al., 2007, 2008).

Long-term lower-temperature simulation experiments are impossible in the laboratory and thermal experimental studies have to be time-limited. Therefore, there is inevitably some disparity between the simulation experiments and the real buried carbonates reservoirs. In the most of the previous simulation experiments, hydrogen sulfide or elemental sulfur was usually directly (Kiyosu and Krouse, 1990, 1993; Cross et al., 2004) or indirectly (Pan et al., 2006) added to the experimental systems in order to initiate TSR. Especially, Pan et al. (2006) have conducted the simulation experiments between gaseous hydrocarbons and sulfates. In their experiments, gaseous hydrocarbons were prepared by kerogen pyrolysis experiments. It should be noted that all their gaseous pyrolysates samples contain H2S. The amount of H2S in the selected nine small capsules ranges from 0.01 mmol/g TOC to 0.67 mmol/g TOC. When a sulfate is the only sulfur source, the reactions between hydrocarbons and sulfates have been performed in the laboratory only at temperatures in excess of 300°C. Geologically significant reaction rates were experimentally measured only above about 350°C (Yue et al., 2005, 2006; Ding et al., 2007, 2008a, 2008b, 2008c, 2010a; Zhang, S. C. et al., 2008; Zhang, T. W. et al., 2007, 2008). Based on the present analytical methods and theoretical studies, it is impossible to realize the reaction between natural gas (dry and free of sulfur) and magnesium sulfate at 100–200°C in the laboratory. The reaction between natural gas (dry and free of sulfur) and magnesium sulfate may have occurred below 300°C, but its reaction extent should be very tiny at low experimental temperatures. In fact when experimental temperatures are below 300°C, it is hard to detect H2S or any possible products of TSR in our experiments. To realize the reaction of natural gas (dry and free of sulfur) and magnesium sulfate, it is necessary to further increase the simulation temperature. Furthermore, the evident carbon isotopic fractionation in the laboratory demands greater reaction conversions of TSR. Therefore, the present experimental temperatures inevitably exceed the natural diagenetic carbonate reservoirs.

According to many geological case studies and theoretical reviews (Amurskii et al., 1977; Machel, 1995, 2001; Worden and Smalley, 1996; Worden et al., 1996, 2000; Seewald, 2003; Cai et al., 2001, 2004), the replacement of anhydrite by calcite occurred during TSR. Carbonates (particularly calcite and dolomite), H2S, CO2, H2O, element sulfur, metal sulfides and solid bitumen have been found in association with TSR settings (Machel, 2001). Carbonates, H2S, CO2 and H2O generally are regarded as the primary inorganic reaction products in TSR system. But the composition and types of TSR products could be altered or changed under different diagenetic environments. For example, the presence of alkali earth metals often results in the formation of carbonates, particularly calcite and dolomite. Other carbonates, i.e., ankerite, siderite, witherite, strontianite, may form if the respective metal cations are available (Machel, 2001). Ding et al. (2007) carried out a series of thermal simulation experiments and found calcium sulfate could be reduced by natural gas to produce calcium carbonate. In the present study, magnesium sulfate was used as an oxidant of natural gas, thus magnesite is justifiably concluded as the one of solid products in TSR system. Pan et al. (2006) did not analyze solid minerals after the oxidation experiment, and they deduced that CO2 could partly precipitate as MgCO3 during the experiment under the consideration that the oxidation extent of C2, components was substantially high while the amount of CO2 and the ratio of CO2/(CO2+2CnH2n+2) were substantially low in comparison with the experiment using Fe2O3. Our simulation experiments temperatures are evidently higher than those of Pan et al. (2006) because the natural gas sample is free of sulfur. The initiation of TSR inevitably demands higher threshold temperature for TSR. The range of simulation temperatures (450–570°C) is much higher than the decomposition temperature for MgCO3 (402°C). So, MgCO3 did not survive after experiments. According to the analysis methods of FT-IR and XRD, MgO is produced during TSR process, and it may be derived for the decomposition of MgCO3. Therefore, it is justifiably de-
duced that MgCO$_3$ should have ever existed in the reaction system of natural gas and magnesium sulfate. In the diagenetical environments, magnesite may be formed by the oxidation of natural gas by MgSO$_4$.

Kiyosu (1980) and Kiyosu and Krouse (1990) reported black precipitates as reaction products of laboratory experiments. Kelemen et al. (2008) characterized of solid bitumen samples associated with TSR or thermal chemical alteration using X-ray Photoelectron Spectroscopy (XPS). Data referring to formation of solid bitumen in natural environments are shown by Sassen (1988) for reservoirs of the Smackover formation and by Powell and Macqueen (1984) related to a carbonate-hosted ore deposit. Pan et al. (2006) have conducted the simulation experiments between gaseous hydrocarbons and sulfates, but they did not analyze solid products after the oxidation experiment. In the present work, some black material was observed in the solid products. After calcinations at 500°C in the muffle, the black material became white. Therefore, the black deposit probably corresponded to be solid bitumen. Highly aromatic, insoluble solid bitumens may develop in reservoir rock either by thermal chemical alteration (TCA) or thermochemical sulfate reduction (TSR) (Machel et al., 1995). This suggested that solid bitumen produced in the present experiments might be derived from TSR or TCA that are beyond the scope of the current work. The purpose of calcination is to remove the excessive solid bitumen from the solid phase after simulation experiments, thus the other solid products can be clearly characterized by the present analytical methods, such as FT-IR and XRD.

Kiyosu and Krouse (1989) conducted an experimental study on the reaction of flowing methane with CuO or hematite and found that the produced CO$_2$ was more depleted in $\delta^{13}$C than the reactant methane. Their experiments were performed at high temperatures (400–650°C), under atmospheric pressure, and in the absence of water, conditions strikingly different from those in sedimentary basins. The reactants, reaction conditions and potential reaction mechanism in the experiments of Kiyosu and Krouse (1989) are very different from those of our present study, which may create the different experimental results.

According to the present study, in absence of S species, the initiation of TSR is mainly determined by the amount of water and types of metallic ions. Once a small amount of H$_2$S is generated from the reaction system, the rate of TSR can be further promoted by H$_2$S because TSR is also considered to be an autocatalytic reaction (Orr, 1974, 1977, 1982). According to Machel (2001), there are many potential kinetic factors in diagenetic environments that may enhance or reduce the rate of TSR: the initial total sulfur concentration in solution (including H$_2$S pressure); temperature; pH; Eh; salts of organic acids; metal complexes; catalytic action of metallic ion and of organic compounds such as phenols, aldehydes, aniline, urea, and vanillin; clay minerals; and silica gel. Although it is now clear that increases in temperature and total initial sulfur concentration in solution greatly enhance the overall reaction rate of TSR, the effects of many of factors mentioned above are not well understood and need further investigation. In our experiments TSR is chemically regarded as an oxidation/reduction reaction. The amount of water and types of metallic ions are experimentally determined as important factors for initiation of TSR. Diagenetically TSR is generally considered as a 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 (Worden et al., 2000; Bildstein et al., 2001). At the same time, these steps may be affected by many potential kinetic factors in diagenetic environments mentioned above. Additionally, physicochemical properties of natural gas, magnesium sulfate and water will change with the increasing temperature, which may also to some extent affect the scale of TSR. The results of the simulation experiments were obtained in a relatively idealized system of TSR precluding many complex factors in the diagenetic environment. The temperatures of simulation experiments were also higher than those of the factual oil & gas reservoirs. Although the present results of the simulation experiments could not yet be directly applied to the geological settings, they are theoretically important for the understanding of TSR process. Further research on the reaction between sulfates and natural gas will be investigated on the basis of simulation experiments in the next work.

**CONCLUSIONS**

Natural gas can react with MgSO$_4$ to produce H$_2$S, CO$_2$, MgO and solid bitumen as the main products of TSR. The gas dryness, the gas-souring index and the extent of reaction parameter positively correlated with temperature. The extent of acidiﬁcation and oxidation of natural gas are intensified as TSR proceeds. There are positive correlations between $\delta^{13}$C values of CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ with the increasing temperature and an inverse correlation between $\delta^{13}$C values of CO$_2$ and temperature, which is caused by kinetic carbon isotope fractionation. During TSR, $^{13}$C–H bonds and $^{12}$C–$^{32}$C bonds of natural gas are preferentially cracked, leading to an enrichment of $^{13}$C in the residual CH$_4$, C$_2$H$_6$ and C$_3$H$_8$. The carbon isotopic fractionation observed in the simulation experiment is consistent with the previous findings in the dry gas TSR provinces.
The presence of a small amount of water can effectively enhanced the oxidation of MgSO₄ through increasing the number of Lewis acid centers scattered on the surface of the sulfates. The catalytic role of a metallic ion in TSR process is controlled by at least three factors: the charges of a metallic ion, the radius of a metallic ion and the number of Lewis acid centers scattered on the surface of the sulfates. The first two factors are associated with the nature of a metallic ion. The last factor is largely determined by the amount of water in a TSR system. A small amount of water and metallic ions with more charges and short radius may effectively initiate TSR.

Acknowledgments — This work was supported by the National Natural Science Foundation of China (Ratification No. 40902034) and Research Start-up Funds of Yangtze University.

REFERENCES
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