Disproportionation and thermochemical sulfate reduction reactions in S–H₂O–CH₄ and S–D₂O–CH₄ systems from 200 to 340 °C at elevated pressures

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Abstract

Elemental sulfur, as a transient intermediate compound, by-product, or catalyst, plays significant roles in thermochemical sulfate reduction (TSR) reactions. However, the mechanisms of the reactions in S–H₂O–hydrocarbons systems are not clear. To improve our understanding of reaction mechanisms, we conducted a series of experiments between 200 and 340 °C for S–H₂O–CH₄, S–D₂O–CH₄, and S–CH₄–1m ZnBr₂ systems in fused silica capillary capsules (FSCCs). After a heating period ranging from 24 to 2160 h (hrs), the quenched samples were analyzed by Raman spectroscopy. Combined with the in situ Raman spectra collected at high temperatures and pressures in the S–H₂O and S–H₂O–CH₄ systems, our results showed that (1) the disproportionation of sulfur in the S–H₂O–CH₄ system occurred at temperatures above 200 °C and produced H₂S, SO₄²⁻, and possibly trace amount of HSO₄⁻; (2) sulfate (and bisulfate), in the presence of sulfur, can be reduced by methane between 250 and 340 °C to produce CO₂ and H₂S, and these TSR temperatures are much closer to those of the natural system (<200 °C) than those of any previous experiments; (3) the disproportionation and TSR reactions in the S–H₂O–CH₄ system may take place simultaneously, with TSR being favored at higher temperatures; and, (4) in the system S–D₂O–CH₄, both TSR and the competitive disproportionation reactions occurred simultaneously at temperatures above 300 °C, but these reactions were very slow at lower temperatures. Our observation of methane reaction at 250 °C in a laboratory time scale suggests that, on a geologic time scale, methane may be destroyed by TSR reactions at temperatures >200 °C that can be reached by deep drilling for hydrocarbon resources.

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1. INTRODUCTION

The thermochemical sulfate reduction (TSR) reaction is a thermally-driven, abiological reduction of sulfate by hydrocarbons at temperatures probably less than 200 °C in natural systems producing combinations of H₂S, CO₂, carbonate minerals (e.g., calcite), elemental sulfur, various

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organic sulfur compounds, and water (Krouse et al., 1988; Machel et al., 1995; Worden and Smalley, 1996; Worden et al., 2000; Machel, 2001; Cross et al., 2004). TSR reactions are considered to be important for the origin of high H2S concentrations in petroleum reservoirs and for the deposition of metal sulfides in ore deposits (Barton, 1967; Orr, 1974, 1977; Anderson, 1975, 1983, 1991, 2008; Powell and Macqueen, 1984; Anderson and Garven, 1987; Machel, 1987; Worden et al., 1995; Worden and Smalley, 1996; Sangster et al., 1998; Sun and Puttmann, 2000; Alonso-Azcárate et al., 2001; Cai et al., 2003, 2005; Garven et al., 2003; Anderson and Thom, 2008; Basuki et al., 2008; Thom and Anderson, 2008). Hydrogen sulfide produced by TSR in oil and gas is considered to be an undesirable component of natural gas, because it not only dilutes the proportion of hydrocarbon gas, but it is also highly toxic and corrosive, resulting in operational, environmental, and treatment-related problems (Worden and Smalley, 1996; Cross et al., 2004; Mougin et al., 2007). Therefore, better understanding of the mechanisms and kinetics of TSR has become a prerequisite to enhance our ability to predict H2S concentrations in gas reservoirs in sedimentary basins and to minimize its unwanted effects (Worden and Smalley, 1996; Pan et al., 2006). Even though geological observations and experimental studies of TSR have been extensive in the past five decades (e.g., Sassen and Moore, 1988; Kiyosu and Krouse, 1993; Cross et al., 2004; Ding et al., 2008; Zhang et al., 2008a; Watanabe et al., 2009), only a limited number of experimental investigations were performed to evaluate the reduction of sulfate by methane. Moreover, most of these experiments (Yue et al., 2005, 2006; Ding et al., 2008; Chou et al., 2008b) were conducted at temperatures much higher than those in the natural geologic settings (Zhang et al., 2008b). Also, it is still controversial whether methane, the predominant component of natural gases, actually participates in natural TSR reactions (Barton, 1967; Krouse et al., 1988; Rhodes, 1994; Machel et al., 1995; Worden and Smalley, 1996, 2004; Worden et al., 2000; Machel, 2001; Cai et al., 2004; Pan et al., 2006; Hao et al., 2008; Zhang et al., 2008b).

There are also uncertainties about the role of elemental sulfur in TSR reactions. Sulfur commonly occurs in sour gas reservoirs in sulfate-bearing carbonate reservoir rocks and it is not clear whether sulfur is a transient intermediate compound or a by-product of TSR reactions (Machel, 1987, 1989; Krouse et al., 1988; Heydari and Moore, 1989; Kiyosu and Krouse, 1993; Machel et al., 1995; Worden and Smalley, 1996; Heydari, 1997; Alonso-Azcárate et al., 2001; Seewald, 2003). Previous geologic studies indicated that elemental sulfur could be produced by reduction of sulfate by C2, hydrocarbons (Orr, 1974; Worden and Smalley, 1996; Worden et al., 1996), and then react with methane and other hydrocarbons to produce H2S and CO2 (Orr, 1974; Machel, 1995; Worden and Smalley, 1996; Heydari, 1997). A number of experimental studies indicated that elemental sulfur plays a significant role in TSR reactions (Toland, 1960; Douglas and Mair, 1965; Kiyosu and Krouse, 1993; Goldhaber and Orr, 1995), but the role of sulfur in TSR reactions in the S–H2O–CH4 system is not known.

We have begun to investigate the mechanisms of TSR reactions using an experimental method in which fused silica capillary capsules (FSCCs) are used as the reaction vessels for investigations of hydrothermal reactions (Shang et al., 2008; Chou et al., 2008b; Yuan et al., 2009). The combination of FSCC and Raman spectroscopy has provided great opportunity for in situ analysis under reaction temperature–pressure conditions. At the beginning of our experiments, we carried out many short-duration (up to 46 min) in situ experiments at temperatures up to 450 °C for the systems containing S, H2O, and CH4 (Yuan et al., 2009). However, due to the slow reaction rate of TSR in these systems, the products of TSR reactions are difficult to detect in these short-duration in situ experiments. Nevertheless, these preliminary results provided guidance for our long-duration experiments, in which the products were analyzed after quenching. Results of both types of experiments will be presented below. The objectives of this study are to (1) better understand the processes of the reactions in the S–H2O–CH4 system and evaluate reaction pathways, (2) evaluate the potential for TSR reactions in the S–H2O–CH4 system at relatively low temperatures, and (3) evaluate the extent of these TSR reactions.

2. EXPERIMENTAL AND ANALYTICAL METHODS

2.1. Experimental methods

Fused silica capillary capsules (FSCCs), prepared from capillaries purchased from Polymicro Technologies, LLC (http://polymicro.com), were used as the reactors in this study. The sample loading procedures, similar to those of Chou et al. (2008a) and Shang et al. (2009), include the following steps: (1) the sample capsules were prepared by first loading the elemental sulfur (99.9999%, Atomergic Chemetals Corp.) from one end of a fused silica tube (0.3 mm OD, 0.1 mm ID, ~6 cm long), and sealing this end in a hydrogen flame; (2) for samples containing D2O, the silica tube loaded with elemental sulfur was dried at 50 °C for 12 h to remove H2O possibly incorporated during loading; (3) deionized water, 1m ZnBr2 solution, or D2O (99.96 atom% D, Sigma–Aldrich Co.) was loaded from the open end of the tube and centrifuged to the closed end; and (4) the open end of the tube was connected to a vacuum line, and after air in the sample tube was evacuated, methane (99.99%, Air Products, Inc. Lot No. 122701-2) was loaded cryogenically by immersing the sealed end of the tube in liquid nitrogen at about 0.1–0.2 MPa methane pressure in the vacuum line for a few minutes, and then sealing the open end of the tube with a hydrogen flame while the enclosed end was still frozen in liquid nitrogen under vacuum (Fig. 1).

For short duration experiments, capsules containing S–H2O and S–H2O–CH4 were heated in a USGS-type heating stage from room temperature to 410 °C for up to 46 min. Raman spectra were collected in situ at high temperature to look for evidence of rapid reactions in these systems. These experiments provided critical evidence for the limited extent of back reactions during quenching of long-term experiments in these systems.
For the long duration experiments, capsules were heated in cold-sealed pressure vessels (CSPVs) at one atmosphere external pressure, and sample temperatures (accurate to ± 3 °C) were monitored by K-type thermocouples with a digital meter. Raman spectra were collected from the quenched FSCCs at room temperature.

2.2. Raman analysis

Raman spectra were acquired with a JY/Horiba LabRam HR Raman system, using 532.06 nm (frequency doubled Nd:YAG) laser excitation, a 40 × Olympus objective with 0.25 numerical aperture, and a 600 grooves/mm grating with a spectral resolution of about 2 cm⁻¹. An approximately 20 mW laser light was focused on a central level of the horizontal tube during the measurement. Raman spectra were collected from 50 to 4200 cm⁻¹ for various lengths of time with one to five accumulations per spectrum.

The emission line of a helium–neon (He–Ne) laser at 632.817 nm was collected simultaneously with the Raman spectra. Its peak position at 2992.52 cm⁻¹ relative to the red light (532.06 nm line of the Nd:YAG laser was used as a calibration reference, such that the real peak positions (t_{\text{red}}) of the reactants and products can be derived from the measured peak positions of the sample (t_{\text{measured}}) and the He–Ne laser light (t_{\text{red}}) by the following relationship (Lu et al., 2007):

\[
{t_{\text{measured}}} \times \frac{1}{t_{\text{measured}}} - v_{\text{red}}}
\]

(1)

Based on the Raman shifts of CH₄ in the starting vapor phase, the initial sample pressure was calculated by using the following equation (Lu et al., 2007):

\[
P(\text{MPa}) = -0.0148 \times D^3 - 0.1791 \times D^2 - 0.8479 \times D^3 - 1.765 \times D^2 - 5.876 \times D
\]

(2)

where \(D\) (in cm⁻¹) = \(v_p - v_0\), \(v_p\) is the CH₄ peak position obtained from the vapor phase in a FSCC sample at room temperature, and \(v_0\) is CH₄ peak position near zero pressure (~2918 cm⁻¹), obtained from a reference FSCC prepared in our laboratory. During heating, the sample pressure increases, but was difficult to estimate due to unknown thermal expansion of the FSCC under relatively high internal pressure.

2.3. Experiment design

Experiments on the S–H₂O–CH₄ and S–H₂O were conducted to test the roles of various reaction mechanisms involved in TSR reaction that have been proposed in previous publications. The long and short duration experiments provide qualitative evidence for the rates of reaction. Experiments with 1m ZnBr₂ were conducted to test for reaction reversals involving H₂S by removing H₂S as quickly as it formed as ZnS precipitates. We also conducted experiments with D₂O to examine the possible role of water as a source for hydrogen during the formation of H₂S.

Analytical measurements were made by Raman spectroscopy to allow monitoring of reaction progress at progressively higher temperatures in the same sample without opening the sample capsule. This prevented any possible oxidation of reaction intermediates by exposure to air. Although other analytical methods have much lower detection limits, Raman spectroscopy is the only method that allows non-destructive observation of changes in reactant and product concentrations in situ at elevated temperature and pressure.

3. RESULTS

The experimental conditions and results are summarized in Table 1. Annotated spectra are shown in Figs. 2–11. Detailed results for each system are as follows:

3.1. The S–H₂O–CH₄ system

The Raman spectra of long duration experiments collected from the aqueous and vapor phases of the samples containing S–H₂O–CH₄ quenched from 200, 250, and 340 °C are shown in Figs. 2 and 3, respectively. These figures show that the Raman signals of SO₄²⁻ (~980 cm⁻¹) in the aqueous phase and H₂S (~2606 cm⁻¹) in the vapor phase were detected in the quenched sample that reacted at 200 °C for 24 h. In the aqueous phase of the 200 °C sample (Fig. 3), there is a shoulder at 1050 cm⁻¹ on a broad band for silica glass that suggests HSO₄⁻ is possibly present at this temperature. When the same capsule was further
heated at 250 °C for 24 h, the spectrum for the aqueous phase (Fig. 3) showed reduction of SO$_4^{2-}$ and HSO$_4^-$ Raman band intensity as well as the presence of H$_2$S. Also, the Raman spectrum of the quenched vapor phase (Fig. 2) showed the presence of CO$_2$ ($\nu_1=2412$ and $\nu_2=1385$ cm$^{-1}$) and H$_2$S. When the same sample capsule was further heated at 340 °C for 96 h, the Raman band intensities of CO$_2$ and H$_2$S in the quenched vapor phase increased significantly and the SO$_4^{2-}$ and HSO$_4^-$ bands in the quenched aqueous phase disappeared.

### Table 1

**Experimental conditions and products detected by Raman spectroscopy.**

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Starting condition</th>
<th>T (°C)</th>
<th>Duration (h)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>S–CH$_4$–H$_2$O</td>
<td>2914.22</td>
<td>17.64</td>
<td>24</td>
<td>SO$_4^{2-}$, H$_2$S</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>24</td>
<td>SO$_4^{2-}$, HSO$_4^-$, H$_2$S, CO$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>96</td>
<td>H$_2$S, CO$_2$</td>
<td></td>
</tr>
<tr>
<td>S–CH$_4$–1m ZnBr$_2$</td>
<td>2915.68</td>
<td>10.49</td>
<td>40</td>
<td>SO$_4^{2-}$, HSO$_4^-$, CO$_2$</td>
</tr>
<tr>
<td>S–CH$_4$–D$_2$O</td>
<td>2914.37</td>
<td>16.86</td>
<td>40</td>
<td>SO$_4^{2-}$, CO$_2$, D$_2$S</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>40</td>
<td>SO$_4^{2-}$, DSO$_4^-$, CO$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2160</td>
<td>CO$_2$, D$_2$S, H$_2$S</td>
<td></td>
</tr>
</tbody>
</table>

* The lengths of all fused silica capillary capsules are about 10 mm, and the initial ratios between vapor and aqueous phase are about 1:2.

* Calculated from Eq (2).

---

**Fig. 2.** Raman spectra collected from the vapor phase of a quenched FSCC containing S, H$_2$O, and CH$_4$, after heating at 200, 250, and 340 °C for 24 to 96 h at each temperature. Also shown is the Raman spectrum of the initial sample at 22 °C. The peak at 2992.52 cm$^{-1}$ is a calibration signal from a He–Ne laser of 632.817 nm wavelength. The peak at 2328 cm$^{-1}$ resulted from N$_2$ in air.

**3.2. In situ experimental results of the systems S–H$_2$O and S–H$_2$O–CH$_4$**

Short duration *in situ* Raman spectra for S–H$_2$O system were recorded for the aqueous phase and the homogenized phase (Fig. 4) and the vapor phase and the homogenized phase (Fig. 5). The time spans at the specified temperatures were shown in Figs. 4 and 5. In the aqueous phase the Raman band of H$_2$S was observed after 18 min at temperatures of 250 °C and higher. Soon after L–V homogenization at 369 °C, weak Raman signals of HSO$_4^-$ and SO$_2$ can be detected. The band for SO$_2$ increases in intensity on further heating, but the weak band for HSO$_4^-$ disappears. During cooling, the Raman signal for SO$_2$ became weaker, and only weak Raman signals of SO$_4^{2-}$ and H$_2$S can be detected 1 day after cooling to room temperature. In the vapor phase (Fig. 5), the Raman bands of H$_2$S and SO$_2$ can be detected at temperatures above 250 and 320 °C, respectively. During cooling, the reduction of Raman signals of SO$_2$ can be observed, and only weak Raman signals of H$_2$S can be detected 1 day after cooling to room temperature.
Fig. 3. Raman spectra collected from the aqueous phase of a quenched FSCC containing S, H₂O, and CH₄ after heating at 200, 250, and 340 °C for 24 to 96 h at each temperature. Also shown is the Raman spectrum of the initial sample at 22 °C. The small shoulder at 1050 cm⁻¹ for the spectra at 200 °C indicates the presence of HSO₄⁻ near or below the detection limit. The peak at 2992.52 cm⁻¹ is a calibration signal from a He–Ne laser of 632.817 nm.

Fig. 4. *In situ* Raman spectra collected from a FSCC containing S and H₂O during heating and cooling in a USGS heating–cooling stage. The spectra shown are for the aqueous phase below the homogenization temperature (∼369 °C) and also for the homogeneous phase above 369 °C. The time spans at the specified temperatures were shown. Note the disproportionation of S to produce H₂S (2593 cm⁻¹), SO₂ (1148 cm⁻¹), and possibly HSO₄⁻ (1050 cm⁻¹) during heating, and the disappearance of SO₂ after cooling to room temperature. The insert shows the SO₄²⁻ (980 cm⁻¹) signal in the aqueous phase at room temperature. The signals at 1240 and 1430 cm⁻¹ were from unknown S-bearing species and the signal at 2992.52 cm⁻¹ is calibration signal from a He–Ne laser of 632.817 nm.
Fig. 5. *In situ* Raman spectra collected from FSCC containing S and H₂O during heating and cooling in a USGS heating–cooling stage. The spectra shown are for the vapor phase below the homogenization temperature (~369 °C) and also for the homogeneous phase above 369 °C. The time spans at the specified temperatures were shown. The insert shows the SO₂ (1146 cm⁻¹) signal in the homogeneous phase at 378 °C. For other information, see Fig. 4.

Fig. 6. *In situ* Raman spectra collected from a FSCC containing S, H₂O and CH₄ during heating and cooling in a USGS heating–cooling stage. The spectra shown are for the aqueous phase below the homogenization temperature (~366 °C) and also for the homogeneous phase above 366 °C. The time spans at the specified temperatures were shown. Note the formation of CO₂ and H₂S during heating. The insert shows the CO₂ (1285 and 1387 cm⁻¹) signals in the homogeneous phase at 400 °C. The peak at 2992.52 cm⁻¹ is a calibration signal from a He–Ne laser of 632.817 nm.
In situ Raman spectra collected from the aqueous phase (together with the homogenized phase) and the vapor phase (together with the homogenized phase) of the S–H2O–CH4 system were shown in Figs. 6 and 7, respectively. In the aqueous phase (Fig. 6), the Raman bands of H2S can be observed at temperatures above 250°C, but those of SO4^2- or

Fig. 7. In situ Raman spectra collected from a FSCC containing S, H2O and CH4 during heating and cooling in a USGS heating-cooling stage. The spectra shown are for the vapor phase below the homogenization temperature (~366°C) and also for the homogeneous phase above 366°C. The time spans at the specified temperatures were shown. Note the formation of CO2 and H2S during heating. The inserts show the H2S (2604 cm^{-1}) and CH4 (2580 cm^{-1}) signals in the vapor phase at 260°C, and the CO2 (1285 and 1387 cm^{-1}) signals in the homogeneous phase at 400°C. The peak at 2992.52 cm^{-1} is a calibration signal from a He–Ne laser of 632.817 nm.

In situ Raman spectra collected from the aqueous phase (together with the homogenized phase) and the vapor phase (together with the homogenized phase) of the S–H2O–CH4 system were shown in Figs. 6 and 7, respectively. In the aqueous phase (Fig. 6), the Raman bands of H2S can be observed at temperatures above 250°C, but those of SO4^2- or

Fig. 8. Raman spectra collected from the aqueous phase of a quenched FSCC containing S–CH4–1m ZnBr2 after heating at 250 and 300°C for 40 h at each temperature. The shoulder at 1050 cm^{-1} for the spectrum at 250°C clearly indicates the presence of HSO4^- at this temperature, but it disappeared at 300°C. Also note the reduction of both Raman signals for SO4^2- (980 cm^{-1}) and CH4 (2910 cm^{-1}). The peak at 2992.52 cm^{-1} is a calibration signal from a He–Ne laser of 632.817 nm.
HSO$_4^-$ cannot be detected during heating and cooling. After L–V homogenization at 366 °C, the Raman signals of CO$_2$ can be detected at 400 °C. In the vapor phase (Fig. 7), the Raman bands of H$_2$S can be detected at temperatures above 260 °C, but that of SO$_2$ cannot be detected during heating and cooling.

Fig. 9. Raman spectra collected from the vapor phase of a quenched FSCC containing S–CH$_4$–1m ZnBr$_2$ after heating at 250 and 300 °C for 40 h at each temperature. Also shown is the Raman spectrum of the initial sample at 22 °C. The insert shows the increase of CO$_2$ signals from 250 to 300 °C. The Raman signal at 2332 cm$^{-1}$ was from N$_2$ in air. The peak at 2992.52 cm$^{-1}$ is a calibration signal from a He–Ne laser of 632.817 nm.

Fig. 10. Raman spectra collected from the aqueous phase of a quenched FSCC containing S–D$_2$O–CH$_4$ after heating at 250 and 300 °C for 40 to 2160 h at each temperature. Also shown is the Raman spectrum of the initial sample at 22 °C. Note the presence of DSO$_4^-$ (1051 cm$^{-1}$) and D$_2$S (1880 cm$^{-1}$) at 250 °C. Significant TSR at 300 °C was indicated by the top two spectra showing the consumption of both CH$_4$ and SO$_4^{2-}$ and the production of D$_2$S. The peak at 2992.52 cm$^{-1}$ is a calibration signal from a He–Ne laser of 632.817 nm.
3.3. The S–1m ZnBr₂–CH₄ system

Results of experiments for S–1m ZnBr₂–CH₄ system are shown in Figs. 8 and 9. Raman signals for SO₄²⁻ and CO₂ can be detected, respectively, in the aqueous (Fig. 8) and vapor (Fig. 9) phases quenched from 250 and 300°C. Moreover, the intensity of SO₄²⁻ and HSO₄⁻ (1050 cm⁻¹) signals decreased significantly from 250 to 300°C, and the intensity of CO₂ signal increased from 250 to 300°C. No significant amount of H₂S was detected due to the formation of dark ZnS precipitates.

3.4. The S–D₂O–CH₄ system

Results of the experiments for S–D₂O–CH₄ system at 250 and 300°C are presented in Figs. 10 and 11, showing that Raman signals can be detected for SO₄²⁻ and DSO₄⁻ in the aqueous phase and also weak signals for CO₂ in the vapor phase, but neither H₂S nor D₂S Raman signals were detected in the sample quenched from 250°C. After heating the same capsule at 300°C for 40 h, the Raman spectra showed the presence of CO₂ (1283 and 1385 cm⁻¹) and H₂S in the vapor phase (Fig. 2). The reduction of SO₄²⁻ Raman band intensity in the aqueous phase (Fig. 3) as well as the presence of H₂S, indicate the occurrence of TSR:

\[
4S + 4H₂O \rightarrow SO₄²⁻ + 3H₂S + 2H⁺. \tag{3}
\]

However, the Raman signals of CO₂ were not detected in this capsule, indicating no or limited TSR reaction in this system at 200°C in 24 h. When the same capsule was further heated at 250°C for 24 h, the Raman signals collected from the quenched sample showed the presence of CO₂ (~1283 and ~1385 cm⁻¹) and H₂S in the vapor phase (Fig. 2). The reduction of SO₄²⁻ Raman band intensity in the aqueous phase (Fig. 3) as well as the presence of H₂S, indicate the occurrence of TSR:

\[
SO₄²⁻ + 2H⁺ + CH₄ \rightarrow CO₂ + H₂S + 2H₂O. \tag{4}
\]

There is limited evidence for the presence of HSO₄⁻ in the aqueous phase (Fig. 3) at 250°C. When the same sample capsule was further heated at 340°C for 96 h, the Raman band intensities of CO₂ and H₂S in the quenched vapor phase increased significantly with the disappearance of SO₄²⁻ and HSO₄⁻ signals in the quenched aqueous phase, indicating near completion of the TSR reaction.

Previous experiments on TSR reaction showed that the rate of sulfate reduction increases in the presence of hydrogen sulfide (e.g., Zhang et al., 2008a). This appears to be a catalytic effect of H₂S on TSR reaction resulting from the reaction between sulfate and H₂S to produce elemental sulfur (Feely and Kulp, 1957; Orr, 1974, 1977; Dinur et al., 1980; Powell and Macqueen, 1984; Goldhaber and Orr, 1995; Machel et al., 1995; Heydari, 1997; Seewald, 2003; Truche et al., 2009), which then reacted with methane or other hydrocar-

4. DISCUSSION

4.1. Evidence of reactions and mechanisms

The experimental results show that the Raman signals of SO₄²⁻ (~980 cm⁻¹), HSO₄⁻ (1050 cm⁻¹), and H₂S (~2606 cm⁻¹) were detected in the quenched S–H₂O–CH₄ sample that reacted at 200°C for 24 h (Figs. 2 and 3). These products are the result of the disproportionation reaction of sulfur, similar to the hydrolysis reaction of native sulfur described by Toland (1960) and Robinson (1973):

\[
4S + 4H₂O \rightarrow SO₄²⁻ + 3H₂S + 2H⁺. \tag{3}
\]

Fig. 11. Raman spectra collected from the vapor phase of a quenched FSCC containing S–D₂O–CH₄ after heating at 250 and 300°C for 40 to 2160 h at each temperature. Also shown is the Raman spectrum of the initial sample at 22°C. The insert shows the increase of CO₂ signals from 250 to 300°C. The peak at 2992.52 cm⁻¹ is a calibration signal from a He–Ne laser of 632.817 nm.
bons and water to produce CO₂ and H₂S (Orr, 1974; Seewald, 2003). Toland (1960) suggested that the catalysis of TSR reaction by low valence sulfur species is more effective at lower pH conditions, although the experiments of Davis et al. (1970) indicate that this reaction is only possible at relatively high temperature conditions. Trudinger et al. (1985) pointed out that the sulfite–sulfide reaction was inhibited by the presence of organic matter. Recently, the experimental studies of Zhang et al. (2008a) suggested that this mechanism may not be important for natural TSR. In situ Raman spectroscopy of S–H₂O system at elevated temperature and pressure showed that the intensities of Raman signals of SO₂ and H₂S increased with increasing temperature in the absence of methane, indicating that the disproportionation reactions of sulfur (reactions 3 and 4, above) are enhanced at elevated temperatures (Figs. 4 and 5, Yuan et al., 2009). In addition, in situ Raman spectra collected from S–H₂O–CH₄ (from 22 to 400 °C) showed that the Raman signals of SO₂⁻ and HSO₄⁻ were not measurable at elevated temperature and pressure (Figs. 6 and 7, Yuan et al., 2009), indicating that the reduction or disappearance of the Raman signals of SO₂⁻ and HSO₄⁻ in S–CH₄–H₂O system occurred at elevated temperature rather than during or after quench. Therefore, the extent of the reaction between H₂S and SO₂⁻ may be very low in S–CH₄–H₂O system under our experimental conditions, and the processes of the catalysis of TSR reaction by low valence sulfur species were probably different from those suggested by previous studies.

Worden and Smalley (1996) and Pan et al. (2006) studied the reaction among sulfur, water, and methane and suggested the following reaction for the consumption of methane and the production of H₂S and CO₂:

\[4S + CH₄ + 2H₂O → CO₂ + 4H₂S.\]  

(5)

Chen et al. (2009) argued that such reactions between sulfur and hydrocarbons are strictly not a TSR reaction because sulfur rather than sulfate was involved in the reaction. They proposed that reactions in sulfur–hydrocarbon systems are based on catalysis by sulfur radicals. Although Orr (1982) pointed out that the hydrolysis of sulfur may compete with the reaction between sulfate and hydrogen sulfide in the presence of low concentrations of oxidizable organic matter, he did not further discuss the TSR reaction in these systems.

Although reaction (5) does not appear to be a sulfate reduction reaction, this reaction equation can be the result of the sum of two reactions, the disproportionation of sulfur to SO₂⁻ and H₂S (reaction 3) followed by reduction of sulfate by CH₄ (reaction 4). To test whether this mechanism of TSR in the S–H₂O–CH₄ system will produce CO₂, H₂S, and H₂O, we conducted similar experiments for samples containing S, CH₄, and 1m ZnBr₂ solution at 250 and 300 °C. By adding ZnBr₂ we effectively excluded the possibility that the loss of SO₂⁻ was due to reversal of the disproportionation reaction between SO₂⁻ and H₂S (reaction 3) in these experiments. The ZnBr₂ removes H₂S as a ZnS precipitate, as soon as H₂S forms during sulfur disproportionation. The results of these experiments are shown in Figs. 8 and 9. Raman signals for SO₂⁻ and CO₂ can be detected, respectively, in the aqueous (Fig. 8) and vapor (Fig. 9) phases quenched from 250 and 300 °C. Moreover, the intensity of SO₂⁻ signal decreased significantly from 250 to 300 °C, and the intensity of CO₂ signal increased from 250 to 300 °C. No significant amount of H₂S was detected due to the formation of dark ZnS precipitates. This result shows that the loss of SO₂⁻ from the sample that was quenched from 300 °C was due to the TSR reaction rather than the reaction between SO₂⁻ and H₂S (i.e., the reverse reaction of the hydrolysis of sulfur). This conclusion is also supported by the corresponding increase in the Raman signal for CO₂ in the quenched FSCC. Therefore, it can be further concluded that the disappearance of SO₂⁻ and the increase of CO₂ and H₂S for the S–H₂O–CH₄ sample heated to 340 °C, as shown in Figs. 2 and 3, may be ascribed to the TSR reaction between sulfate and methane at elevated temperature rather than the reaction between SO₂⁻ and H₂S or the reverse reaction of the hydrolysis of sulfur, as shown by reaction (3).

4.2. Evidence that the TSR reaction and competitive disproportionation reactions occurred simultaneously at elevated temperatures

To further test that disproportionation reactions of sulfur are important parts of the TSR process in the S–H₂O–CH₄ system at elevated temperatures, experiments were conducted in the S–D₂O–CH₄ system at 250 and 300 °C. As shown in Figs. 10 and 11, Raman signals can be detected for SO₂⁻ and DSO₄⁻ in the aqueous phase and also weak signals for CO₂ in the vapor phase, but neither H₂S nor D₂S Raman signals were detected in the sample quenched from 250 °C, which indicates that both the disproportionation reaction of sulfur and the TSR reaction were very slow at this temperature. After heating the same capsule at 300 °C for 40 h, Raman spectra showed the increase of CO₂ signals and the presence of D₂S in the quenched sample but not H₂S. The presence of D₂S and the increase of CO₂ signals demonstrate the increase of both the disproportionation reaction of sulfur and the TSR reaction. When the same capsule was further heated at the same temperature (300 °C) for another 2160 h (90 days), H₂S can be clearly detected with a significant increase of D₂S and CO₂ (Figs. 10 and 11), indicating the degrees of both TSR and disproportionation reactions increase significantly after long reaction times. Finally, we note that CH₄D can be detected in the vapor phase after 90 days of reaction (Fig. 11). This appears to be a result of isotopic exchange between D₂O or D₂S and CH₄ at elevated temperature.

4.3. Comparison with other laboratory studies

Geologic studies of a number of petroleum reservoirs with evidence of TSR alteration of hydrocarbons indicated that these reactions required temperatures on the order of 140 °C (Worden et al., 1995) for extensive reaction. However, all well documented laboratory simulations of TSR require temperatures >300 °C (see discussion in Zhang et al., 2008b) even in the presence of potential catalysts. None of these studies have indicated that CH₄, the least reactive hydrocarbon, participated in the reactions. The reactions observed in our experiments occurred at temperatures much lower than those reported previously. Furthermore,
we have demonstrated that the disproportionation reaction of sulfur, a key step of TSR in S–H₂O–CH₄ system, occurs in the laboratory at temperatures as low as 200 °C to produce SO₄²⁻ and H₂S, as described by reaction (3). At temperatures above 250 °C, the sulfate and bisulfate are reduced by methane to produce CO₂ and H₂S.

Although our observation of formation of HSO₄⁻ during some reaction sequences (e.g., Fig 8 in the presence of ZnBr₂ and Fig. 10 in the presence of D₂O) could imply that the pH in these experiments was very low, HSO₄⁻ is only present as a transient trace component in S–H₂O–CH₄ system (Fig. 3). Acid catalysis is known to enhance reaction rates of organic compounds, but there is no evidence that enough bisulfate formed in the S–H₂ system to cause the bisulfite–sulfate ratio to buffer pH to very low values. Furthermore, we have observed in other experiments in the 10 N H₂SO₄–CH₄ system at 300 °C for half a year (Shang et al., unpublished data) that there was no obvious TSR reaction in this acid system. This clearly shows that low pH is not a critical factor in the occurrence of TSR reaction in the systems studied in this work.

A recent study of a high temperature (215 °C) reservoir documented extensive TSR reactions with hydrocarbons including hydrocarbon gases (Mankiewicz et al., 2009). However, the ¹³C composition of CH₄ showed only a small range of variation suggesting that CH₄ had participated in TSR reaction to only a limited extent. Our observation of methane reaction at 250 °C at laboratory time scales suggests that, at geologic time scales, methane may be destroyed by TSR reactions at temperatures >200 °C that can be reached by deep drilling for hydrocarbon resources.

5. CONCLUSIONS

(1) The disproportionation of sulfur in the S–H₂O–CH₄ system occurred at laboratory temperatures above 200 °C and produced H₂S, SO₄²⁻, and traces of HSO₄⁻.

(2) Sulfate (and bisulfate), in the presence of sulfur, can be reduced by methane between 250 and 340 °C to produce CO₂ and H₂S, and these TSR temperatures are much closer to those of the natural system (<200 °C) than those of any previous experiments.

(3) The disproportionation of sulfur and TSR reactions in the S–H₂O–CH₄ system may take place simultaneously, with TSR reaction being favored at higher temperatures.

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