

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

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Thermochemical reduction of MgSO_4 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 MgSO_4 to produce H_2S , CO_2 , 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: MgSO_4 , natural gas, thermochemical sulfate reduction (TSR), carbon isotope fractionation, reaction mechanism

INTRODUCTION

The increasing demand for oil and natural gas has made H_2S -bearing gas an important choice for China's energy supply. H_2S is generally an undesirable component of natural gas. Where present, H_2S not only can critically affect the economic proportion of hydrocarbon gas, but is highly toxic to lives and corrosive for production equipment. H_2S -rich gases (>10% H_2S) 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 H_2S -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 H_2S , used as an initiator in the other experiments (Goldhaber and Orr, 1995). The amount of H_2S 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 MgSO_4 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 MgSO_4 and discuss the catalysis of metallic ions in the process of TSR.

The results may further improve our understanding of thermochemical origin of H_2S in natural gas.

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

T (°C)	Chemical composition of the gaseous products (%)													
	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₅ H ₁₂	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₆ H ₁₄	H ₂	CO ₂	CO	H ₂ S
25	78.560	11.847	BD	4.323	BD	1.038	0.715	0.257	0.281	0.107	BD	2.872	BD	BD
450	86.436	8.633	0.007	1.029	0.054	0.005	BD	BD	BD	BD	0.197	3.432	0.188	0.019
480	88.542	5.609	0.055	0.145	0.141	BD	BD	BD	BD	BD	1.212	3.989	0.253	0.054
510	89.820	3.354	0.095	0.009	0.187	BD	BD	BD	BD	BD	1.520	4.439	0.432	0.144
540	90.016	1.502	0.141	0.001	0.202	BD	BD	BD	BD	BD	1.793	5.033	1.027	0.285
570	90.313	0.130	0.181	BD	0.212	BD	BD	BD	BD	BD	2.085	5.146	1.178	0.755

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

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 (Hubei province, China) and its composition was shown in Table 1. The reactor was heated to 450°C, 480°C, 510°C, 540°C and 570°C directly and the heating time was of 168 h. Temperature was controlled to within 1°C of the set value, and was monitored using a pair of thermocouples secured to the outer and inner walls of the autoclave. The initial pressure was about 3 MPa at room temperature and the final pressure of the reaction system ranged from 12 to 20 MPa. When the desired reaction temperature or time was reached, the autoclave was withdrawn from the oven, air cooled for 30 min, and then rapidly cooled to room temperature by quenching in water. After the quartz glass cylinder with solid products was taken out of the autoclave, first put into an oven to be heated at 120°C for about 6 h to remove water, and then calcinated at 500°C in the muffle.

Characterization

The properties of the products were characterized by microcoulometry, gas chromatography, FT-IR, XRD and GC-C-IRMS methods, respectively. The microcoulometry with a model of WK-2B (Jiangsu, China) was used to determine total sulfur of gaseous products which were injected into the microcoulometer 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 60°C. The flow rates of air, nitrogen, and sample gas were 40 mL/min, 160 mL/min, and 30 mL/min, respectively.

Composition of gaseous reaction products was determined with an Agilent 6890 (Agilent Technologies, USA) gas chromatograph, equipped with a thermal-conductivity detector, a flame-ionization detector, 3 RTX-65TG capillary columns (30 m × 0.25 mm i.d., film thickness 0.1 μm) and 2 packed columns (30 m × 0.32 mm i.d., film thickness 0.25 mm). The identification of peaks was achieved by comparing their retention times with those of standards from Nu Chek Prep (Elysian, MN, USA) and Sigma-Aldrich (Sigma, St. Louis, MO, USA). Peaks were integrated using Hewlett-Packard Chem Station software. The oven temperature was programmed at 50°C for 3 minutes; heated to 100°C with a heating rate of 5°C/min; then reached 180°C with a heating rate of 10°C/min and stayed at this temperature for 3 minutes. The detector temperature was set at 250°C. N₂ was used as carrier gas.

A small amount of the solid samples collected from the surface of the reaction products after calcinations were finely ground, mixed with dried potassium bromide (Merck, spectroscopic grade) in the ratio of 1:100 and pressed into pellets for FT-IR determination. At room temperature, FT-IR spectra were obtained in diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) mode using the micro sampling cup of a Spectra-Tech diffuse reflectance accessory (about 2 mg dried sample) against a KBr background on a Nicolet 750 FT-IR spectrometer (ThermoNicolet Corporation, USA, DTGS detector; Nichrome source; KBr beamsplitter). The FT-IR spectra were treated with the Thermo Electron soft-

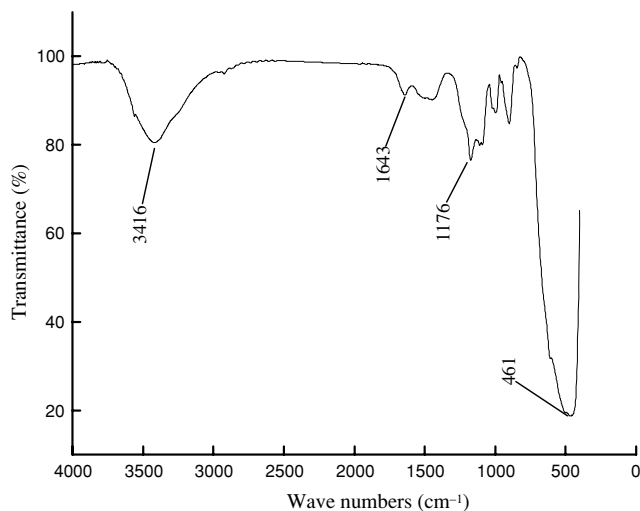


Fig. 1. FT-IR spectrum of solid reaction products at 510°C after calcinations.

ware OMNIC v. 7.0, by averaging 32 scans at a spectral resolution of 4 cm⁻¹ under dried nitrogen flow (10 cm³/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 2θ 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–Kα radiation source (λ = 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 ¹³C/¹²C 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.,

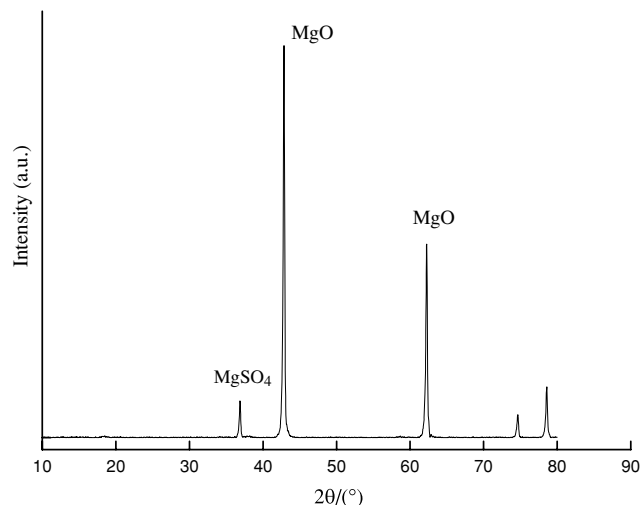


Fig. 2. X-ray patterns of the solid products at 510°C after calcinations.

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 CO₂ 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 CO₂ (99.998% purity) inter-calibrated against NBS22 and expressed in the delta notation versus PDB carbonate:

$$\delta^{13}\text{C} = 10^3(R_{\text{sa}}/R_{\text{st}} - 1). \quad (1)$$

Where $R = {}^{13}\text{C}/{}^{12}\text{C}$ of sample (sa) and standard (st), respectively. The $\delta^{13}\text{C}$ of NBS22 relative to PDB is -29.4‰ (Zheng and Chen, 2000). The analysis of $\delta^{13}\text{C}$ 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

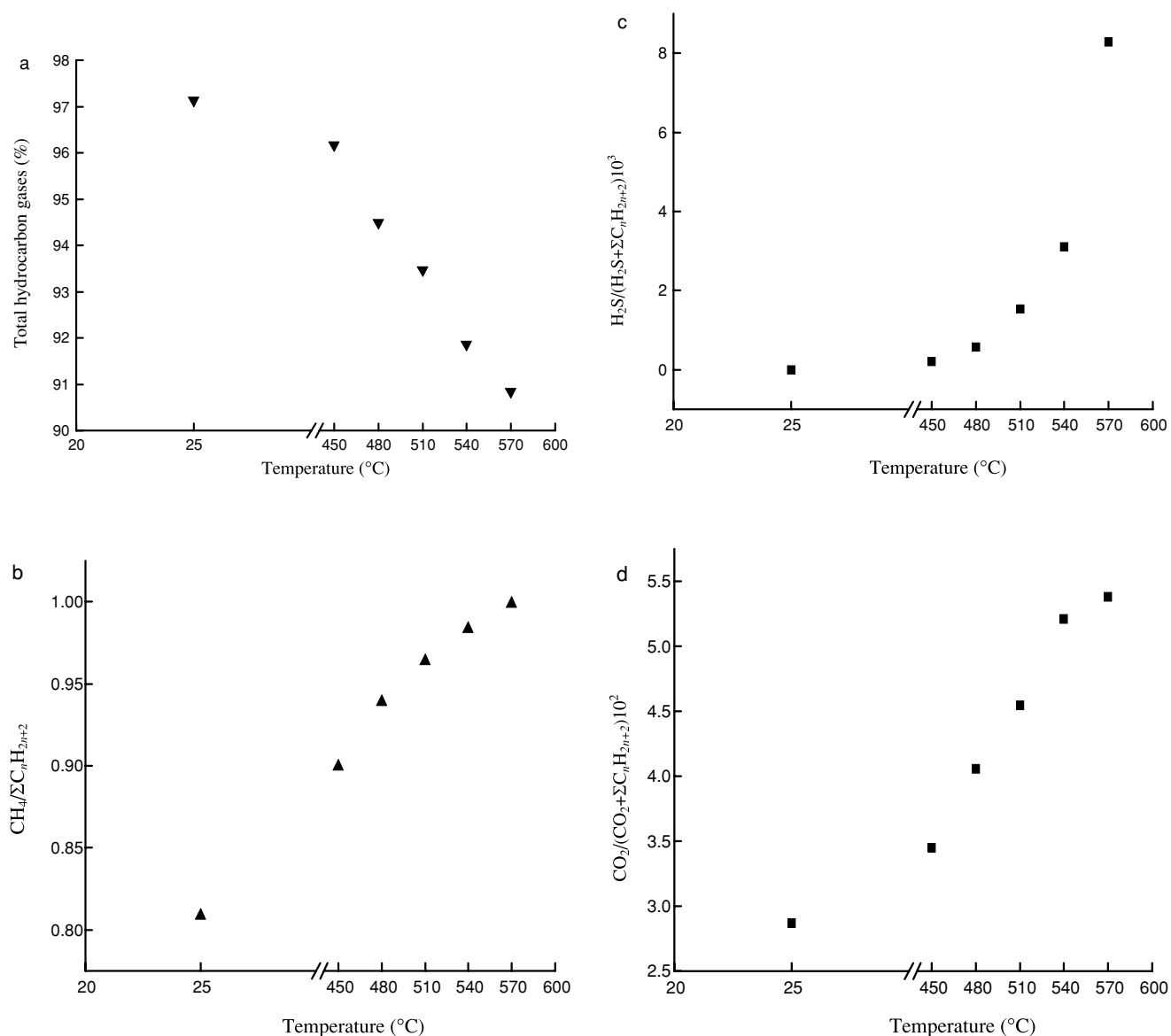


Fig. 3. Relationships between several natural gas parameters and temperature. (a) Total hydrocarbon gases vs. temperature; (b) Gas dryness vs. temperature; (c) Gas souring index vs. temperature; (d) Extent of reaction parameter vs. temperature.

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 MgSO₄ 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 CH₄, C₂H₆, C₃H₈, C₄H₁₀ and CO₂ besides a little of C₅H₁₂ and C₆H₁₄ (Table 1). With the increasing temperature, C₄–C₆ hydrocarbons disappear first of all, and the amounts of C₂H₆ and C₃H₈ are decreasing gradually. The ratio of CH₄ in the gas composition increases as other hydrocarbons decrease or disappear. It is obvious in Table 1 that the content of H₂S increases as temperature grows, which indicates that high temperatures are favorable for the production of H₂S. Although the origi-

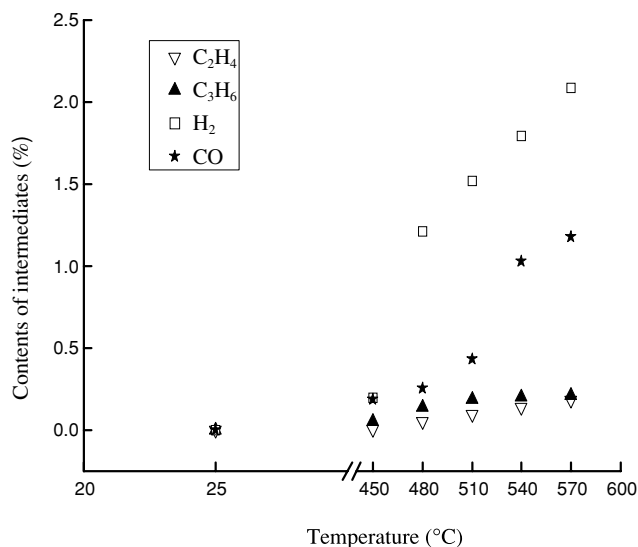


Fig. 4. Contents of alkenes, H_2 and CO with increasing temperature.

nal natural gas sample contains a little CO_2 , the pressure of gaseous products at room temperature is always higher than the initial pressure of natural gas sample in the autoclave. Combining with the ideal gas law and Table 1, it is evident that the number of moles of CO_2 increases as temperature grows. Additionally, no H_2S or increasing CO_2 was found in the blank tests without $MgSO_4$. So, H_2S and CO_2 are products of oxidation of natural gas by TSR, which confirm the previous findings (Machel *et al.*, 1995; Machel, 2001).

A variety of indices have been used in order to track changes in the natural gas chemistry. Gas dryness, defined as $CH_4/\sum C_nH_{2n+2}$, is used to monitor the evolution of the hydrocarbon gas population (Worden and Smalley, 1996). A “gas souring index”, defined as $H_2S/(H_2S+\sum C_nH_{2n+2})$, is used to monitor the changing amounts of H_2S and hydrocarbons in natural gas (Worden *et al.*, 1995). The ratio $CO_2/(CO_2+\sum C_nH_{2n+2})$ is used as an “extent of reaction parameter” (Krouse *et al.*, 1988). Relation between (1) total hydrocarbon gases and temperature; (2) between gas dryness and temperature; (3) between gas souring index and temperature; (4) and between extent of reaction parameter and temperature are shown in Figs. 3a, 3b, 3c and 3d, respectively. The decreasing total hydrocarbon gases and the increasing gas dryness are associated with increasing temperature (Figs. 3a and 3b). Additional blank tests without $MgSO_4$ were carried out at 450–570°C using a natural gas sample (initial pressure 3 MPa) and 10 ml of distilled water. With the increasing temperature, the ratio of CH_4 in the gas composition also increased in the blank tests without $MgSO_4$, but its extent of growth (e.g., 0.482% at 570°C) much

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

T (°C)	Carbon isotopic composition of the gaseous products (‰, PDB)			
	$\delta^{13}CH_4$	$\delta^{13}C_2H_6$	$\delta^{13}C_3H_8$	$\delta^{13}CO_2$
25	−40.4	−27.5	−24.5	−15.5
450	−39.5	−24.0	−23.1	−22.5
480	−39.4	−23.6	−19.8	−24.0
510	−38.5	−23.0	BD	−25.1
540	−38.3	−20.7	BD	−31.4
570	−38.0	−20.1	BD	−31.9

The gas composition at 25°C is the original composition of natural gas.

BD: below detection level.

lower than that of the simulation experiments using $MgSO_4$ (e.g., 11.753% at 570°C). So, thermal cracking of natural gas only mildly affects the composition of natural gas. The increasing gas dryness in the simulation experiments using $MgSO_4$ should be mainly attributed to TSR. Gas souring index and the extent of reaction parameter positively correlate with temperature (Figs. 3c and 3d). These results indicate that the extent of acidulation and oxidation of natural gas are gradually intensified as TSR proceeded.

Positive relationships were observed between the content of alkenes, H_2 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 $MgSO_4$, the thermal cracking of natural gas or even the secondary reaction between solid bitumen, hydrogen and water under high temperatures. H_2 was mainly from the decomposition of natural gas. CO might be the intermediate of TSR or from the reduction of part of CO_2 by H_2 . The above analysis of the reaction products leads to the inference that the oxidation of natural gas by $MgSO_4$ had occurred. H_2S , CO_2 , MgO and solid bitumen are the main products of the reaction between natural gas and $MgSO_4$.

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 $\delta^{13}C$ 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 $\delta^{13}C$ values of C_3H_8 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 $\delta^{13}C$ values of methane and ethane, $\delta^{13}C$ values of CO_2 become more negative during the process of TSR. Carbon in the last

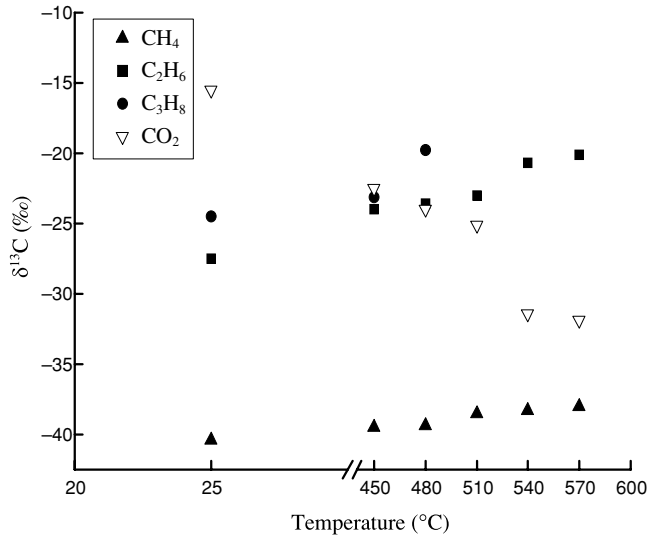
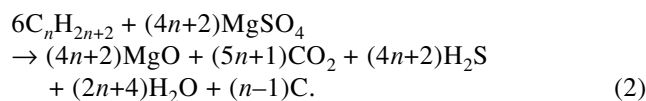


Fig. 5. Variations of $\delta^{13}\text{C}$ values of CH_4 , C_2H_6 and CO_2 with increasing temperature.

formed CO_2 is nearly 9.4‰ lighter than the first formed CO_2 (Table 2, Fig. 5). These above patterns evidently illustrate that TSR has induced an alteration of the carbon isotopes of the remaining methane and ethane, which is caused by kinetic carbon isotope fractionation of natural gas during TSR. The increase of $\delta^{13}\text{C}$ values for methane and ethane could have resulted from the relatively greater extent of ^{12}C preferential depletion by TSR, with the residual methane and ethane thus becoming more enriched in ^{13}C opposite to carbon isotope of CO_2 . The carbon isotopic fractionation observed in the simulation experiments is consistent with the previous findings in the dry gas TSR provinces (Machel, 1995; Worden and Smalley, 1996).

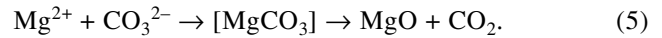
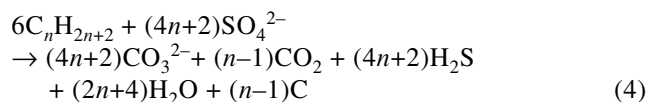
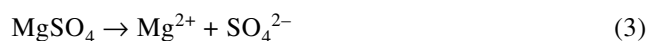
Tentative study of reaction mechanism

Based on the results of simulation experiments, the reaction between natural gas and magnesium sulfate could be written as the general reaction Eq. (2).



Where, $n = 1, 2, 3 \dots$

The reaction of natural gas- MgSO_4 may consist of some elementary steps as follows:



When water is vaporized under high temperatures and then adheres to the surface of magnesium sulfate, the ionic bond of $\text{Mg}^{2+}-\text{SO}_4^{2-}$ can easily be broken and the reactive SO_4^{2-} is given out as is shown in Eq. (3). Because the chemical structure of SO_4^{2-} is most stable, Eq. (4) may be a rate-controlled step of the whole process of TSR. Mg^{2+} from the dissolved magnesium sulfate can be united with CO_3^{2-} produced in Eq. (4), which leads to the formation of MgCO_3 . MgCO_3 is thermodynamically unstable under high temperatures. In fact, MgCO_3 begins to decompose and produce MgO and CO_2 at 402°C (Dean, 1991). So Eq. (5) may be a very fast process at the range of simulation temperatures ($450\text{--}570^\circ\text{C}$). Although the rate of reaction of natural gas- SO_4^{2-} is slow as is discussed above, once few of CO_3^{2-} is generated from TSR system, it will be quickly transformed to CO_2 according to Eq. (5).

In the reaction system, by inductive effect, Mg^{2+} 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 enhanced the oxidation of MgSO_4 . 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 $\text{H}_2\text{O}/\text{MgSO}_4$, 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, Na_2SO_4 , Na_2SO_3 or CaSO_4 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 Mg^{2+} , and the radius of K^+ and Na^+ is longer than that of Mg^{2+} . 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_2S -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: $CaSO_4 \cdot 2H_2O$), 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_2S 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_2S 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_2S 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 diagenetic carbonates formed. These carbonate minerals are always associated with calcium sulfate in the precursor deposits. In the presence of formation 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 be seen in dedolomitization processes and the accompanying formation of epsomite ($MgSO_4 \cdot 7H_2O$) 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 or 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-chromatographic data (Krouse *et al.*, 1988; Manzano, 1995; Rooney, 1996; Manzano *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+∑C_{*n*}H_{2*n*+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 diagenetic 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 minerals 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 ^{13}C than the reactant methane. Their experiments were performed at high temperatures ($400\text{--}650^\circ\text{C}$), 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_2S is generated from the reaction system, the rate of TSR can be further promoted by H_2S 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_2S pressure); temperature; pH; Eh; salts of organic acids;

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 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_2S , 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 acidulation and oxidation of natural gas are intensified as TSR proceeds. There are positive correlations between $\delta^{13}\text{C}$ values of CH_4 , C_2H_6 and C_3H_8 with the increasing temperature and an inverse correlation between $\delta^{13}\text{C}$ values of CO_2 and temperature, which is caused by kinetic carbon isotope fractionation. During TSR, $^{12}\text{C}\text{--H}$ bonds and $^{12}\text{C}\text{--}^{12}\text{C}$ bonds of natural gas are preferentially cracked, leading to an enrichment of ^{13}C in the residual CH_4 , C_2H_6 and C_3H_8 . The carbon isotopic fractionation observed in the simulation experiments 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 MgSO_4 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.

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