Thermal simulation experiments of saturated hydrocarbons with calcium sulfate and element sulfur: Implications on origin of H₂S

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Temperature-programmed simulation experiments of saturated hydrocarbons with calcium sulfate and element sulfur were compared in this study. Based on the variation analysis of the yields and evolvement features of gaseous hydrocarbon (C_1—C_5) and inorganic gaseous CO_2, H_2 and H_2S, the reaction mechanisms were analyzed and discussed. In the calcium sulfate-saturated hydrocarbon system, H_2S was produced by a small quantity, which indicates this reaction belongs to the low-degreed thermal sulfate reduction (TSR) and is featured of self-pyrolysis. In the sulfur-saturated hydrocarbon system, the heated sulfur becomes sulfur radical, which has strong catalysis capability and can fasten the cracking of C—H bond in the alkyl group in the saturated hydrocarbons. As a result, the cracking of C—H bond leads to the yields enhancement of CO_2 and H_2, and at the same time, H_2S was produced since the cracked hydrogen can be instantly combined with sulfur radical. Therefore, this reaction in the sulfur-hydrocarbon system belongs to the catalysis of sulfur radical. Furthermore, the promoted pyrolysis effects of C_{6+} hydrocarbons by sulfur radical in the low-temperature stage in the sulfur-hydrocarbon system, together with the consumption effects of gaseous hydrocarbon in the high-temperature stage in the calcium-hydrocarbon system, result in the crossed phenomenon of the gaseous hydrocarbon yields curves.

H₂S with properties of high corrosion and toxicity plays a hugely harmful role in the hydrocarbon exploration and development. Worldwide, H₂S widely exists in the natural gas reservoirs and its concentration can reach up to 90%[1]. It is widely accepted that TSR is the direct cause for the high H₂S content[1−4]. According to previous studies, the presence of sulfur can obviously enhance the TSR rate[5,6]. Many organic compounds from kerogen, crude oil, asphaltene, gaseous hydrocarbon, and dissolved gaseous hydrocarbons were believed to be the organic reduction agent, while some sulfates, for example, gypsum and anhydrite widely occurring in some geological conditions, are thought to be oxidation agent that occurred in the sub-terranean TSR reaction[7].

Despite many geological case studies[8−12], only a few simulation experiments were reported. The simulation experiments performed in the foreign countries were mainly by sulphate and pure organic matter in aqueous solution, whereas more simulation experiments between solid sulphate and gaseous hydrocarbon under anhydrous conditions[13−15] were undertaken in China. Basically, a few reports were involved in the reaction be-

tween liquid hydrocarbons and solid calcium sulfate.

Sulfur widely exists in the source rock and reservoir conditions, especially abundant in the gypsum-salt depositional environment[16]. The S—S bond in the element sulfur lightly tends to be cracked into sulfur radical, which can increasingly promote the pyrolysis of the organic matter[17] and spontaneously produce H_2S and organic sulfur compounds (OSC)[7,18]. Generally, the more the organic sulfur content, the lower the average activation energy[19]. Meanwhile, the content of organic sulfur compounds in the source rock shows a negative correlation with the average activation energy[20]. Sulfur can promote the cracking of kerogen[21,22]. Comparatively, little simulation experiment is involved in the effect of sulfur to crude oil cracking. In this study, based on the comparison of variation of the gaseous component yields between the calcium sulfate-hydrocarbon system and the sulfur-hydrocarbon system, the possible reaction mechanisms in these two thermal simulation experiments were investigated and discussed.

1 Sample and simulation experiment

Saturated hydrocarbon fraction comes from crude oil in the Che571 well in the Chezhen Sag of the Jiyang Depression. Through asphaltene precipitation and silica gel column chromatographic separation, saturated hydrocarbon fraction was obtained by elution of n-hexanes. GC chromatogram of the saturated hydrocarbon fraction shows a bimodal distribution of n-alkanes, in which the carbon numbers range from nC_9 to nC_{36} and maximum at nC_{17} and nC_{25}, respectively. No sulfur exists in the saturated hydrocarbon fraction. Sulfates and elemental sulfur are purchased from the Sigma-Aldrich Co. and the quantity of sulfur was designed approximately equal to that in the calcium sulfate.

The simulation experiments performed in the closed-gold tube system and the detailed methods are referred in many previous studies[23−26]. In the simulation experiments, temperature-programmed system was used and the constant heating was set at different duration under 330, 360, 390, 420, 450, 480, 510, 540, 570 and 600°C, respectively. Full load heating was used between the room temperature and the initial 330°C, and then heated by a rate of 20°C/h. The experiment system was performed under pressure of 50 MPa and 50.0 μL deionized water was added in all the samples.

GC analyses were performed using an Agilent 6890N GC equipped with a Wasson ECE system. The loaded gold tubes were sealed under a vacuum closed atmosphere, then conducted the gas into the chromatogram instrument with an on-off valve and made component analysis with an automatic sampling system. Helium and nitrogen were employed as the carrier gas. The oven temperature started at 70°C and held for 5 min, then ramped to 130°C at a rate of 15°C/min and again ramped to 180°C at 25°C/min, held for 4 min. The quantification was carried out with external standard.

2 Results

The gaseous hydrocarbons (C_1—C_5) and inorganic gases (CO_2, H_2 and H_2S) produced in the simulation experiments can be measured by double channel and double detector system. In this study, variations of the yields of gaseous components at different temperatures and their evolution characteristics (Table 1, Figure 1) are investigated and discussed in order to explore the possible reaction mechanisms.

2.1 Variations of the gaseous hydrocarbon yields

(1) CH_4 (Figure 1(a)). The methane yields in the two reaction systems both increased with increasing simulation temperature. The methane gases in the sulfur-hydrocarbon and $CaSO_4$-hydrocarbon system are produced obviously at 390 and 420°C, respectively. Their yields in the two systems become equal at 500°C and tend to be enhanced even at 570°C. The methane yield in the sulfur-saturated hydrocarbon system is higher at the low-temperature stage whereas the methane yield in the $CaSO_4$-hydrocarbon system is higher at the high-temperature stage.

(2) C_2H_6 (Figure 1(b)). The ethane yields in the two reaction systems both increased with increasing simulation temperature. The ethane yields in the sulfur-hydrocarbon and $CaSO_4$-hydrocarbon systems are also produced obviously at 390 and 420°C, respectively. The ethane yields become equal at about 465°C and the curve slopes of two reactions both tend to be maximum at 570°C. Therefore, it can be predicted that the yields will be decreased when the temperature is higher than 570°C. The ethane yield in the sulfur-saturated hydrocarbon system is higher at the low-temperature stage whereas the ethane yield in the $CaSO_4$-saturated hydro-
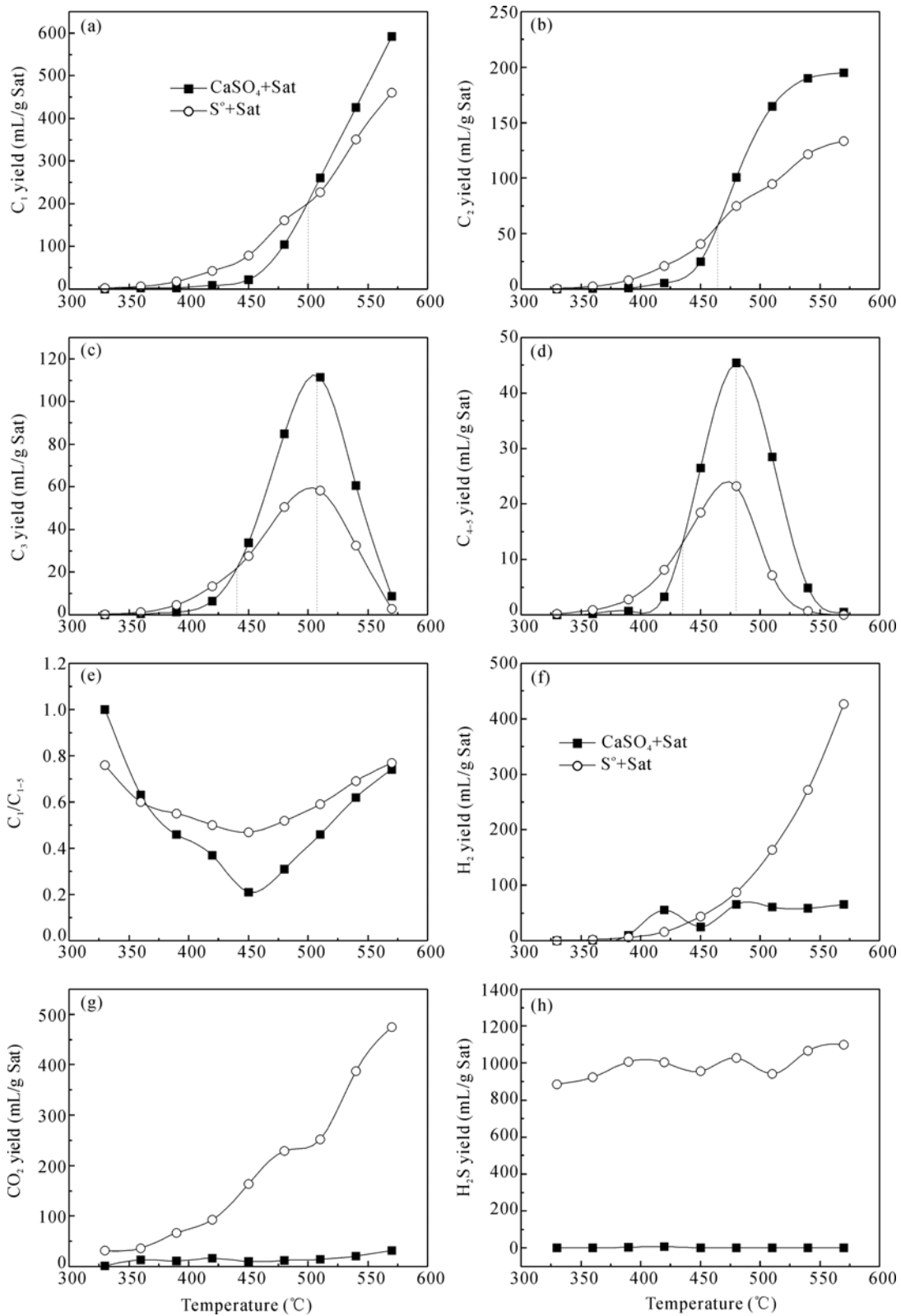
Figure 1 Variations of yields of gaseous hydrocarbons in the calcium sulfate and elemental sulfur with saturated fraction of crude oil in the thermal simulation experiments.

Table 1 Variations of the yields for organic and inorganic gases in the two thermal simulation experiments[a]

Saturated hydrocarbon + $CaSO_4 \cdot 2H_2O$ + H_2O									Saturated hydrocarbon + S° + H_2O								
T (℃)	Yield (mL/g)							C_1/C_{1-5}	T (℃)	Yield (mL/g)							C_1/C_{1-5}
	C_1	C_2	C_3	C_{4-5}	H_2	CO_2	H_2S			C_1	C_2	C_3	C_{4-5}	H_2	CO_2	H_2S	
330	0.3	0.0	0.0	0.0	0.0	1.2	0.0	1.00	330	3.1	0.5	0.3	0.2	0.2	31.7	886.2	0.76
360	2.6	0.7	0.6	0.2	1.0	13.1	2.4	0.63	360	7.0	2.3	1.4	0.9	1.7	36.1	923.7	0.60
390	2.5	1.0	1.2	0.7	9.8	11.4	3.8	0.46	390	18.6	7.8	4.6	2.8	5.7	66.9	1007.8	0.55
420	8.8	5.4	6.5	3.3	55.6	16.4	6.2	0.37	420	42.8	21.0	13.4	8.1	15.9	92.9	1004.4	0.50
450	22.4	24.9	33.9	26.5	24.8	10.0	2.1	0.21	450	78.1	40.5	27.5	18.5	44.1	163.8	957.2	0.47
480	104.2	100.9	84.9	45.4	65.1	11.9	2.0	0.31	480	161.2	74.7	50.6	23.2	87.6	229.3	1027.9	0.52
510	260.7	164.6	111.5	28.5	60.7	14.0	2.0	0.46	510	226.9	94.6	58.3	7.1	163.9	252.2	941.8	0.59
540	425.4	189.9	60.5	4.9	58.4	20.8	1.9	0.62	540	350.7	121.7	32.5	0.7	272.2	387.7	1067.8	0.69
570	591.4	195.0	8.7	0.5	65.5	31.7	1.8	0.74	570	459.9	133.3	2.8	0.0	426.8	474.5	1100.7	0.77
600	—	—	—	—	—	—	—	—	600	—	—	—	—	—	—	—	—

a) "—" stands for the unobtainable data because of break of golden tube. The quantity used in the two reaction systems were about: $CaSO_4 \cdot 2H_2O \approx$ 50.00 mg; S ≈ 9.00 mg; saturated hydrocarbon ≈ 8.50 mg; $H_2O \approx$ 50 μL.

carbon system is higher at the high-temperature stage.

(3) C_3H_8 (Figure 1(c)). The propane yields in the two reaction systems fluctuated with increasing temperature, increased first and decreased later. The propane in the two systems is produced obviously at 390 and 420℃, respectively. The propane yields reached the maximum at 510℃ and the curve before 510℃ is similar to the curve of C_2H_6. Their yields become the same at 440℃, and after that, the yields decrease and reach the lowest at 570℃.

(4) C_{4-5} (Figure 1(d)). The C_{4-5} yield curves of the two reaction systems with increasing temperature increased first and decreased later, similar to that of C_3H_8. The C_{4-5} gaseous hydrocarbons in the two systems start to be produced at 390 and 420℃, respectively. The yields become the same at 435℃ and reach the maximum at 480℃, and then the yields decrease and become the lowest at 570℃.

(5) The variations of the yields of gaseous hydrocarbons can be summarized as following: (a) Variations of the yields in the two systems showed a similar regularity, which increased with increasing temperature at the low-temperature stage. (b) There is a cross in the two yield curves and the crossed temperature for C_1 to C_{4-5} gases showed a declined trend (500, 465, 440 and 435℃, respectively). (c) An inflexion occurred in the yield curves of the C_3H_4 and C_{4-5} gaseous components and the corresponding temperature was decreased (from 510 to 480℃). The yields of C_{3-5} components at the inflexion temperature in the $CaSO_4$-saturated hydrocarbon system are higher than that of the sulfur-saturated hydrocarbon system. (d) The dry coefficient (C_1/C_{1-5})

decreased with increasing temperature before 450℃ and increased after 450℃ as shown in Figure 1(e). The yield of CH_4 is increased during the whole process of thermal simulation, thus, the decrease of dry coefficient before 450℃ mainly comes from the obvious enhancement of C_2-C_5 gases while the increase of dry coefficient after 450℃ apparently results from the consumption of C_2-C_5 gases.

2.2 Variations of the yields of inorganic gases

(1) H_2 (Figure 1(g)). The H_2 yield in the $CaSO_4$-hydrocarbon system was commenced at 390℃ and maintained 60 mL/g at the subsequent temperature (except 450℃). The H_2 yield started to increase obviously at 390℃ and an exponential-type growth with increasing temperature exhibited in the sulfur-saturated hydrocarbon system, reaching up to 426.8 mL/g at 570℃.

(2) CO_2 (Figure 1(f)). The CO_2 yield in the $CaSO_4$-hydrocarbon system increased at 390℃ and was maintained between 10 mL/g and 20 mL/g at the subsequent temperatures. The maximum reaches up to 31.7 mL/g at 570℃. Higher CO_2 yield commenced (31.7 mL/g) at 330℃ and a linear growth with the increasing temperature showed in the sulfur-saturated hydrocarbon system, which reaches up to 474.5 mL/g at 570℃.

(3) H_2S (Figure 1(h)). The H_2S yield in the $CaSO_4$-hydrocarbon system reached the maximum (6.2 mL/g) at 420℃ and increased with the increasing temperature before 420℃, then maintained 2 mL/g. Apparently higher H_2S yield commenced at 330℃ and an almost saturated, balanceable but wavy curve shown in the sul-

fur-hydrocarbon system, which reached up to 1100.7 mL/g at 570℃. It is obvious that huge difference over 500−600 times existed in the H_2S yields of the two systems.

(4) Variations of the yields of the inorganic gas can be summarized as following: on a whole, the yields of inorganic gases in the two systems increased with increasing temperature and reached the maximum at 570 ℃ (the H_2S yield in the $CaSO_4$-hydrocarbon system showed differently). Tremendous difference of the yield for H_2, CO_2 and H_2S showed in the two systems, which one order of magnitude for the yields of the H_2 and CO_2 gases and three orders of magnitude for H_2S gas existed between the sulfur-hydrocarbon system and the $CaSO_4$-hydrocarbon system.
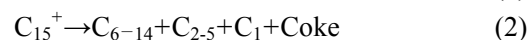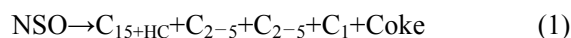
3 Discussion

## 3.1 Reaction mechanisms in the two simulation experiments

Depended on the reactant used in the systems, several possible reaction mechanisms might exist in the two experiments as following: (1) Pyrolysis reaction for hydrocarbons must be taken into account since hydrocarbons were used in the thermal simulation experiment. (2) Thermal Sulfate Reduction (TSR) will be thermodynamically driven forward at high temperature since sulfate with oxidation property and hydrocarbons with reduction property existed in the reactant. (3) Catalytic reaction by sulfur. Sulfur can react with hydrocarbons under thermal condition, which is strictly not TSR reaction since sulfur does not belong to sulfate. The reaction mechanism in the sulfur-hydrocarbon system is greatly different from that in the sulfate-hydrocarbon system, which can be seen in the variations of the yields for the organic and inorganic gases as shown in the following.

3.1.1 Hydrocarbon pyrolysis

With increasing temperature, high molecular-weight hydrocarbons were pyrolyzed into small molecular-weight hydrocarbons because of thermal cracking reaction. The higher the temperature reached and the more duration time prolonged, the more some higher molecular-weight hydrocarbons cracked, and finally gaseous hydrocarbons with lower carbon-number and tar were produced[27−29]. The pyrolysis process of crude oils was concluded in previous studies[29,30] as following:

$$NSO \rightarrow C_{15+HC}+C_{2-5}+C_{2-5}+C_1+Coke \qquad (1)$$
$$C_{15}^+ \rightarrow C_{6-14}+C_{2-5}+C_1+Coke \qquad (2)$$
$$C_{6-14} \rightarrow C_{2-5}+C_1+Coke \qquad (3)$$
$$C_{2-5} \rightarrow C_1+Coke \qquad (4)$$

H_2 is always produced, especially under aqueous condition. Thus, a common formula can be reached as following:

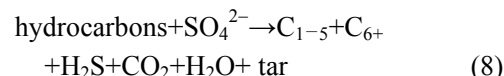$$Saturated\ hydrocarbons \rightarrow C_{1-5}+C_{6+}+H_2+coke \qquad (5)$$
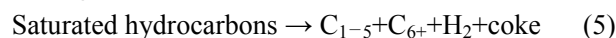
3.1.2 TSR

TSR is a reaction between organic and inorganic reactant, which consumes hydrocarbon and reduces sulfate[31]. TSR can produce a large amount of H_2S, characterized by generation of high content H_2S. The gaseous CH_4, C_2H_6 were proposed to be involved in the TSR reaction with $CaSO_4$ in the studies on the Permian Khuff Formation in Canada[4]:

$$CaSO_4+CH_4 \rightarrow CaCO_3+H_2S+H_2O \qquad (6)$$
$$2CaSO_4+C_2H_6 \rightarrow 3CaCO_3+H_2S+S+CO_2+2H_2O \qquad (7)$$
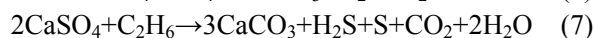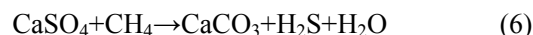
Machel[32] gave a whole reaction formula for TSR:

$$hydrocarbons+SO_4^{2-} \rightarrow C_{1-5}+C_{6+}$$
$$+H_2S+CO_2+H_2O+tar \qquad (8)$$

The selective consumption for hydrocarbons in TSR tends to be higher carbon-numbered components[33,34]. According to theoretical calculation and kinetics simulation, at the same temperature, the possibility for long-chain alkanes reacting with solid $CaSO_4$ was higher than that for short-chain alkane[15].

3.1.3 Catalysis reaction for sulfur

With regard to the reaction between sulfur and hydrocarbons, Orr[35] pointed out the following universal reaction formula when he studied the features of gaseous components and their stable isotopic compositions in the Big Horn Basin, Canada:

$$S + 1.33(-CH_2-) + 2.66H_2O \rightarrow 4H_2S +1.33CO_2 \qquad (9)$$
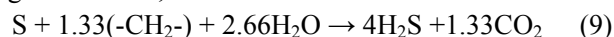
According to the kinetics calculation[33], the activation energies of reaction between sulfur and hydrocarbons will be reduced with increasing carbon numbers. Thus, higher carbon-numbered hydrocarbons will be consumed first by sulfur.

3.2 Analysis on the reaction behavior in the simulation experiment

Under current condition, only gaseous components were measured in this experiment. However, it is important to monitor the variations of gaseous compositions. For example, organic gases represent the degree of hydro-

carbon cracking while inorganic H_2S and CO_2, to some degree, represent the reaction degree of TSR, even though they can also be produced from the reaction between sulfur and hydrocarbons. The yields of gases in the two systems are obviously different, especial for inorganic gases (H_2, CO_2 and H_2S), so the variations of inorganic gases combined with reaction mechanism were analyzed first in this paper.

In addition, a great amount of H_2 was produced in the sulfur-saturated hydrocarbon system in this simulation experiments. However, it seems that H_2 was not associated in previously studied reaction formula in the above-mentioned hydrocarbon cracking, TSR and catalysis reaction of sulfur (eqs. (1)−(9)). Therefore, detailed reaction mechanism involved in the inorganic gases must be analyzed and explained from viewpoint of element transformation and migration.

3.2.1 The cause of variations of the yields of inorganic gases

As mentioned above, high-molecular-weight hydrocarbons were pyrolyzed into lower-molecular-weight components in the pyrolysis process. That is, only the simple chains shortening occurred while no obvious C−H bond cracking happened in pyrolysis process; otherwise, lots of H will be produced in this process. Because the bond energy of C−H bond in a single molecular or in an alkyl group (e.g., 420.5 kJ/mol for ethane) is remarkably larger than the activation energy of high-molecular-weight components (e.g., 230−272 kJ/mol for nC_{18}[36]), C−H bond are not easily cleavaged during the hydrocarbon cracking process. In the calcium sulfate-saturated hydrocarbon system in this study, the yields of H_2S, H_2 and CO_2, and the extent of TSR reaction were very low, which indicates that only hydrocarbon cracking reaction was involved in the whole reaction system. Therefore, no obvious production of H_2 and CO_2 occurred in the reaction.

Several allotropes occurred in elemental sulfur and only rhombic sulfur can exist under the room temperature since its melting point is 112.8℃ and boiling point is 444.7℃. In the element sulfur, eight sulfur atoms are linked by covalent bond. Thus, under the heating conditions, S−S bond of elemental sulfur is easily cracked into sulfur radical in the sulfur-saturated hydrocarbon system. Sulfur radical can easily abstract the H atom from C−H bond, thus, destroying the previous balance and accelerating the cleavage of C−C bond[17]1), which instantaneously lead to the continuous cracking of C−H bond and C−C bond. As a consequence, CO_2 was preferentially produced by combining the cracked carbon with oxygen and exhibited a linear growth of the yield with increasing temperature since the production of CO_2 is only affected by bond cracking (Figure 1(g)).

The H abstracted from C−H bond will preferentially combine with sulfur radical into H_2S, and only redundant H can be used to produce H_2. The large amount of H_2S was produced at the beginning in the sulfur-saturated hydrocarbon system, which comes from the large quantity of sulfur radical and large quantity of H atoms abstracted from the C−H bond. Almost saturated state for the production of H_2S is approached at 330℃ (at that time the conversion percentage is up to 77.3%, mainly controlled by sulfur content, Figure 1(h)). In the subsequent process of increasing temperature, the production of H_2S exhibited a wavy curve due to the equilibrium effects of supplying and consumption of sulfur radical and H atoms.

As for the variations with increasing temperature of the H_2 yield, it shows exponential-type growth, which is neither similar to the linear increase of CO_2 nor similar to the wavy curve of H_2S after the initial saturation state. The real cause can be attributed to the supplying equilibrium effect of sulfur radical and H atoms. Below 420 ℃, the H atoms abstracted from the C−H bond will preferentially and completely combine with sulfur radical into H_2S. As a result, deficient H atoms supplying lead to the un-obvious increase of H_2 yield. Above 420 ℃, large quantity consumption of sulfur radical at the first stage will lead to its deficient supplying and redundant supplying of H atoms; as a consequence, plentiful H_2 was produced and exponential growth curve was exhibited for the yield H_2 gas (Figure 1(f)).

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1) In the classical theory, oil generation is mainly controlled by the bond length of the precursor, while the high sulfur organic matter is influenced by C−S bond. But it can not explain the generation of iso-paraffin in low temperature stage. Lewan (Nature, 1998) pointed out that in the early stage of the thermal mature stage, sulfur radical generated by homolytic reaction of sulfide especially disulfide can get an H from alkyl-group, then break the previous balance and promote the thermal fracture of C−C bond. Molecular simulation results showed that the influence of C−S bond to C in C−C bond which has the primary H and the second H is less than 15 kJ/mol.

From the viewpoint of element transference, the C of CO_2 comes from hydrocarbon thermal cracking, while the O of CO_2 comes from H_2O, or oxygen-contained compounds in the saturated hydrocarbon fraction of crude oil, or some un-removed air in golden tube. H_2O can provide O and H atom in the supercritical state, CO_2 and H_2 can even be derived from the reaction between H_2O and hydrocarbon under geological condition[37]. H atoms can largely come from the cracking of C—H bond in saturated hydrocarbon or small quantity derived from H_2O. As for the source of large quantity of H_2S, most sulfur in H_2S apparently comes from calcium sulfate and elemental sulfur while most H atom mainly comes from cleavage of C—H bond in the saturated hydrocarbon.

According to the simulation experiment results presented in this study, large quantity of H_2S will be produced as long as hydrocarbons and sulfur coexist because of catalysis effect of sulfur radical. Element sulfur exists widely in the source rock and reservoir environment, especially in the gypsum-salt deposits[15]. If only there is large amount of sulfur and good contact relationship, it possibly leads to the production of lots of H_2S. In fact, the melting point of sulfur (112.8℃) is lower than the widely accepted critical temperature (140 ℃) for TSR in many case studies[1,3,4,5,32,38]. Furthermore, the activation of sulfur is higher than that of gypsum and anhydrite under the real geologic conditions. Therefore, the large amount of H_2S in natural gas reservoir is not definitely related to TSR reaction and might be possibly come from catalysis of element sulfur. Observations from the whole section of cores in the Zhaoxin1 and Zhaoxin2 well in the Jinxian Sag, Bohai Bay Basin, revealed that element sulfur was redundantly produced only in the section with indigent organic matter and H_2S can be strongly smelled in the section with abundant organic matter. This proved the negative relationship between sulfur and organic matter and further confirmed the important role of sulfur on the generation of H_2S.
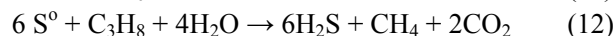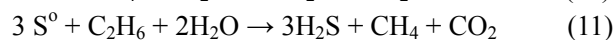
3.2.2 The cause of variations of the yield of organic gaseous hydrocarbon

Based on the above analysis, the yields of C_1 and C_2 increased and the yields of C_{3-5} increased first and decreased later with increasing temperature in the two systems. It is consistent with the reported results of simulation experiments of pure octadecane[36], crude oil[39,40] and coal cracking[41]. Thus, the variations of the yields of gaseous hydrocarbons are mainly controlled by the

self-cracking reaction of saturated hydrocarbons.

During the initial reaction stage, the self-cracking reaction of saturated hydrocarbon and their reactions with calcium sulfate and sulfur in the two systems all preferentially consume C_{6+} liquid hydrocarbon first[15,33,34] and produce some low carbon-numbered gaseous hydrocarbons. This reaction is beneficial to producing gaseous hydrocarbon and leads to the gradual increasing of C_{1-2} and C_{3-5} gaseous hydrocarbons. In the sulfur-saturated hydrocarbon system at the low temperature stage, the sulfur radical accelerate the cracking of saturated hydrocarbons and the generation of gaseous hydrocarbons, and as a result, the yields curve is higher than that in calcium sulfate-saturated hydrocarbon system (Figure 1).

During the later high-temperature stage in the two reaction systems, the yields of C_{4-5} and C_3 both decreased at 480 and 500℃, respectively. The reasons can be explained as following: (1) the previous consumption of C_{6+} liquid hydrocarbon leads to their lacking, which are used to be cracked into C_{3-5}, as a consequence, the C_{3-5} yields decreased. (2) The produced C_{3-5} gaseous hydrocarbons were involved in cracking into C_{1-2} again, which leads to the gradual increase of C_{1-2}. As a result, the production rate of C_{3-5} is less than that of cracking, which leads to the decrease of the C_{3-5} yields. In the calcium sulfate-saturated hydrocarbon system, the variations of the gaseous hydrocarbon yields are mainly controlled by hydrocarbon self-cracking reaction since TSR is weak. However, in the sulfur-saturated hydrocarbon system, more carbon and hydrogen atoms in the C_{6+} liquid hydrocarbons were transferred into CO_2, H_2 and H_2S due to obvious effect of sulfur radical. Thus, the yields of C_1—C_5 gaseous hydrocarbons were obviously lower than that in the calcium sulfate-saturated hydrocarbon system. Furthermore, sulfur can react with CH_4, C_2H_6, C_3H_8[33] as shown in formulae 10, 11 and 12, which aggravates the decrease of C_1—C_5 yields.

$$4\,S^o + CH_4 + 2H_2O \rightarrow 4H_2S + CO_2 \qquad (10)$$
$$3\,S^o + C_2H_6 + 2H_2O \rightarrow 3H_2S + CH_4 + CO_2 \qquad (11)$$
$$6\,S^o + C_3H_8 + 4H_2O \rightarrow 6H_2S + CH_4 + 2CO_2 \qquad (12)$$

4 Conclusions

Based on the results of simulation experiment and reaction mechanism, the following conclusions can be

reached.

(1) Low-degreed TSR reaction occurred in the calcium sulfate-saturated hydrocarbon system since a small quantity of H_2S and CO_2 was produced. Hydrocarbon self-cracking reaction mainly inhabited in this system.

(2) Catalysis reaction of sulfur radical mainly existed in the sulfur-saturated hydrocarbon system since a large quantity of H_2S and CO_2 was yielded. Sulfur radical firstly promotes the cleavage of C－H and C－C bond and the cracked hydrogen radical and sulfur radical instantly were combined into H_2S. Above 420℃, the decreased content of sulfur radical makes more redundant hydrogen radical combining into H_2, which leads to the exponential growth in the H_2 yield curve. Carbon atoms produced from C－H and C－C bond cracking were combined with oxygen into CO_2, which exhibited a linear growth in its yield curve.

(3) The sulfur radical catalysis effect of large molecules in the low-temperature stage and consumption of gaseous hydrocarbon by sulfur were attributed to the crossed phenomenon in the yields curve of gaseous hydrocarbons in the calcium sulfate-saturated hydrocarbon and sulfur-saturated hydrocarbon systems.

(4) The result of the simulation experiment presented in this study shows that sulfur plays an intense and important role in the generation process of H_2S. Sulfur not only can be the intermediate product during TSR reaction, but also can exist as sulfur deposits in the nature. Especially, sulfur was widely occurred in the gypsum-salt sedimentary area with high concentrations of H_2S. All these imply that the large production of H_2S in the nature is not necessarily related with TSR reaction, but it also possibly comes from the catalysis reaction between sulfur and hydrocarbon.

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