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**Reduction of Calcium Sulfate by Activated Carbon under Hydrothermal Conditions:  
Experimental Study and Thermodynamic Assessment**

Kangle Ding<sup>1,\*</sup> and Shasha Wang<sup>2</sup>

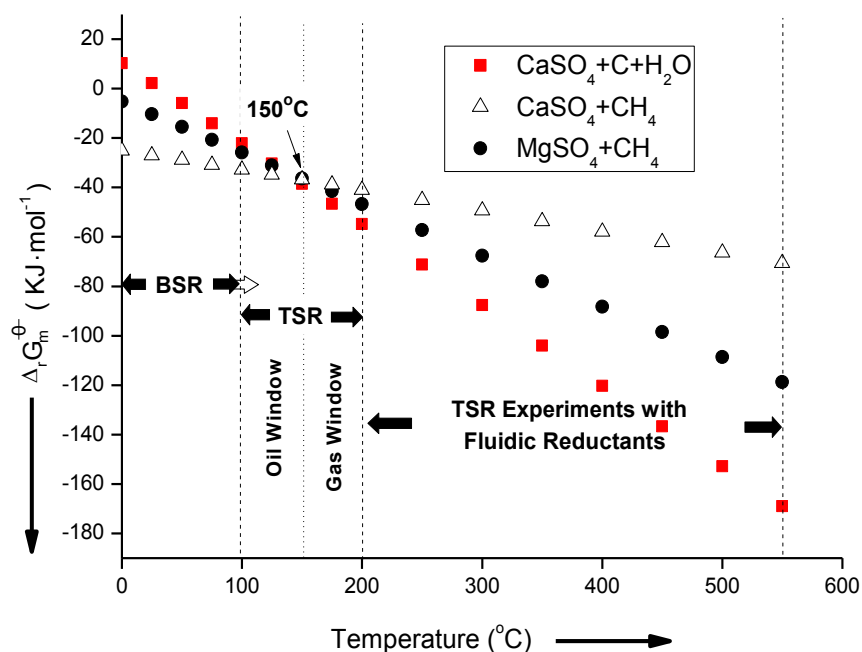
<sup>1</sup>School of Chemistry and Environmental Engineering, Yangtze University, Jingzhou 434023, Hubei, China

<sup>2</sup>Science and Technology Department, Yangtze University, Jingzhou 434023, Hubei, China

Thermochemical sulfate reduction (TSR), an abiological reduction of reservoir sulfates by hydrocarbons, can give rise to highly aromatic, insoluble solid bitumens in many petroliferous basins. Solid bitumens found in association with TSR settings, typically deep-buried carbonate rocks, are well documented in many geological observations from around the world (e.g. Stasiuk, 1997; Machel, 2001). These types of solid bitumens have long been recognized as direct, stable byproducts of TSR, and their presence has not been considered an important factor in the TSR process, in comparison with hydrogen sulfide (H<sub>2</sub>S).

In most of geological observations, traditional reducing agents for TSR mainly consist of branched and n-alkanes, n-alkenes, followed by cyclic and mono-aromatic species, in the gasoline range (e.g. Goldstein and Aizenshtat, 1994; NÖth, 1996; Machel, 2001), but also sometimes involve methane (e.g. Worden and Smalley, 1996; Cai et al., 2004). Fluidic organic compounds, mainly gaseous and liquid hydrocarbons, have generally been used as reducing agents in previous TSR simulations (e.g. Kiyosu and Krouse, 1990, 1993; Goldhaber and Orr, 1995; Cross et al., 2004; Pan et al., 2006; Yue et al., 2006; Ding et al., 2007, 2008, 2010, 2011; Zhang, S. C. et al., 2008; Zhang, T. W. et al., 2007, 2008a, 2008b; Amrani et al., 2008, Chen et al., 2009; Lu et al., 2010). Few investigations have been made concerning solid bitumens as reducing agents for TSR. TSR-bitumen, especially pyrobitumen with fine-grained mosaic needle coke (Stasiuk, 1997) was carbon-rich, hydrogen-poor and generally produces negligible pyrolyzate yields (Kelemen et al., 2010). In the present study, thermochemical reduction of calcium sulfate (CaSO<sub>4</sub>) by activated carbon (C), a model compound for solid bitumen, was conducted under hydrothermal conditions at elevated temperatures. As CaSO<sub>4</sub> is the only sulfur source and water is the only hydrogen source initially present in the simulation experiments, any H<sub>2</sub>S formed must arise from TSR. Thermal simulation experiments and thermodynamic analysis on the system calcium sulfate-activated carbon-water (CaSO<sub>4</sub>-C-H<sub>2</sub>O) were conducted in order to investigate the fate of solid bitumens in deep-buried carbonate reservoirs and the corresponding formation of H<sub>2</sub>S.

According to the experimental results, the threshold temperature for initiating TSR was only 300°C which was lower than most previous TSR simulations using hydrocarbons (340°C-600°C: e.g. Yue et al., 2006; Pan et al., 2006; Ding et al., 2007, 2008, 2010, 2011; Zhang, S. C. et al., 2008; Zhang, T. W. et al., 2007, 2008a, 2008b; Amrani et al., 2008, Chen et al., 2009; Lu et al., 2010). Especially in comparison with hydrocarbons reported in previous field observations and simulation studies, water in the present study became the only hydrogen source for the generation of H<sub>2</sub>S. Based on the experimental results, TSR in system CaSO<sub>4</sub>-C-H<sub>2</sub>O could be written as follows,



**Fig.5** Effect of temperatures on standard Gibbs function of molar TSR in systems CaSO<sub>4</sub>-C-H<sub>2</sub>O, CaSO<sub>4</sub>-CH<sub>4</sub> (Yue et al., 2006; Ding et al, 2007, 2010) and MgSO<sub>4</sub>-CH<sub>4</sub>(Ding et al, 2008, 2010).

The standard Gibbs free energy of molar TSR in system CaSO<sub>4</sub>-C-H<sub>2</sub>O at different temperatures was calculated according to the reaction pathway (1) and shown in Fig.1 which also included our previous thermodynamic studies on the systems CaSO<sub>4</sub>-CH<sub>4</sub> (Yue et al., 2006; Ding et al., 2007, 2010) and MgSO<sub>4</sub>-CH<sub>4</sub> (Ding et al., 2008, 2010).

Fig.1 was divided into three temperature zones, i.e. a BSR zone (0°C -100°C: Goldstein and Aizenshtat, 1994; NÖth, 1996; Machel, 2001), a TSR zone (100°C -200°C: Goldstein and Aizenshtat, 1994; NÖth, 1996; Machel, 2001) and a TSR experiment zone (200°C -600°C: Kiyosu and Krouse, 1990, 1993; Goldhaber and Orr, 1995; Cross et al., 2004; Pan et al., 2006; Yue et al., 2006; Ding et al., 2007, 2008, 2010, 2011; Zhang, S. C. et al., 2008; Zhang, T. W. et al., 2007, 2008a, 2008b; Amrani et al., 2008, Chen et al., 2009; Lu et a., 2010). The absolute

value of Gibbs free energy of the systems  $\text{CaSO}_4\text{-CH}_4$ ,  $\text{MgSO}_4\text{-CH}_4$  and  $\text{CaSO}_4\text{-C-H}_2\text{O}$  increased with increasing temperature (Fig.1), which implied that the increasing temperature was favored. TSR in system  $\text{CaSO}_4\text{-C-H}_2\text{O}$  proceeded spontaneously above  $50^\circ\text{C}$  according to the negative values of Gibbs free energy. In the BSR zone and typical oil reservoirs ( $100^\circ\text{C}$  - $150^\circ\text{C}$ ), the relative thermodynamic possibility for TSR was the system  $\text{CaSO}_4\text{-CH}_4 >$  the system  $\text{MgSO}_4\text{-CH}_4 >$  the system  $\text{CaSO}_4\text{-C-H}_2\text{O}$ . When temperature was above  $150^\circ\text{C}$ , TSR thermodynamically more easily occurred in system  $\text{CaSO}_4\text{-C-H}_2\text{O}$  than in systems  $\text{MgSO}_4\text{-CH}_4$  and  $\text{CaSO}_4\text{-CH}_4$ , which was confirmed by the experimental results. The present results of the simulation experiments are theoretically important for the understanding of the role of solid bitumen during TSR. Further research such as kinetics and reaction mechanism on the system  $\text{CaSO}_4\text{-C-H}_2\text{O}$  will be investigated in the next work.

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### References

- Amrani, A., Zhang, T. W., Ma, Q. S., Ellis, G. S. and Tang, Y. C. (2008) The role of labile sulfur compounds in thermochemical sulfate reduction. *Geochim. Cosmochim. Acta* **72**, 2960-2972.
- Cai, C. F., Xie, Z. Y., Worden, R. H., Hu, G. Y., Wang, L. S. and He, H. (2004) Methane-dominated thermochemical sulphate reduction in the Triassic Feixianguan Formation East Sichuan Basin, China: towards prediction of fatal  $\text{H}_2\text{S}$  concentrations. *Mar. Petr. Geol.* **21**, 1265-1279.
- Chen, T. S., He, Q., Lu, H., Peng, P. A. and Liu, J. Z. (2009) Thermal simulation experiments of saturated hydrocarbons with calcium sulfate and elemental sulfur: implications on origin of  $\text{H}_2\text{S}$ . *Sci. China, Ser. D: Earth Sci.* **52**, 1550–1558.
- Cross, M. M., Manning, D. A. C., Bottrell, S. H. and Worden, R. H. (2004) Thermochemical sulphate reduction (TSR): experimental determination of reaction kinetics and implications of the observed reaction rates for petroleum reservoirs. *Org. Geochem.* **35**, 393-404.
- Ding, K. L., Li, S. Y., Yue, C. T. and Zhong, N. N. (2007) Simulation experiments on thermochemical sulfate reduction using natural gas. *J. Fuel. Chem. Technol.* **35**, 401-406.
- Ding, K. L., Li, S. Y., Yue, C. T. and Zhong, N. N. (2008) Simulation experiments on the reaction system of  $\text{CH}_4\text{-MgSO}_4\text{-H}_2\text{O}$ . *Chin. Sci. Bull.* **53**, 1071-1078.
- Ding, K.L., Li, S.Y., Yue C.T. and Zhong, N.N. (2010) Investigation of two kinds of thermochemical sulfate reduction systems. *Energy Sources, Part A* **32**, 1130-1141.
- Ding, K.L, Wang S.S, Li, S. Y. and Yue, C. T. (2011) Thermochemical reduction of magnesium sulfate by natural gas: insights from an experimental study. *Geochem. J.* **45**. In press.
- Goldhaber, M.B. and Orr, W.L. (1995) Kinetic controls on thermochemical sulfate reduction as a source of sedimentary  $\text{H}_2\text{S}$ . *Geochemical Transformations of Sedimentary Sulfur* (Vairavamurthy, M.A. and Schoonen, M.A.A. eds.), ACS Symposium Series 612, 412-425.
- Goldstein, T.P. and Aizenshtat, Z. (1994) Thermochemical sulfate reduction-a review. *J. Therm. Anal.* **42**, 241-290.

- Kelemen, S. R., Walters, C. C., Kwiatek, P. J., Freund, H., Afeworki, M., Sansone, M., Lambert, W. A., Pottorf, R.J., Machel, H. G., Peters, K. E. and Bolin, T. (2010) Characterization of solid bitumens originating from thermal chemical alteration and thermochemical sulfate reduction. *Geochim. Cosmochim. Acta* **74**, 5305-5332.
- Kiyosu, Y. and Krouse, H. R. (1990) The role of organic-acid in the abiogenic reduction of sulfate and the sulfur isotope effect. *Geochem. J.* **24**, 21-27.
- Kiyosu, Y. and Krouse, H. R. (1993) Thermochemical reduction and sulfur isotopic behavior of sulfate by acetic-acid in the presence of native sulfur. *Geochem. J.* **27**, 49.
- Lu, H., Chen T.S., Liu J.Z., Peng P.A., Lu Z.H. and Ma Q.L. (2010) Yields of H<sub>2</sub>S and gaseous hydrocarbons in gold tube experiments simulating thermochemical sulfate reduction reactions between MgSO<sub>4</sub> and petroleum fractions. *Org. Geochem.* **41**, 1189-1197
- Machel, H. G. (2001) Bacterial and thermochemical sulfate reduction in diagenetic settings: old and new insights. *Sediment. Geol.* **140**, 143-175.
- Nöth, S. (1996) High H<sub>2</sub>S contents and other effects of thermochemical sulfate reduction in deeply buried carbonate reservoirs: a review. *Geol. Rund.* **86**, 275-287.
- Pan, C. C., Yu, L. P., Liu, J. Z. and Fu, J. M. (2006) Chemical and carbon isotopic fractionations of gaseous hydrocarbons during abiogenic oxidation. *Earth Planet. Sci. Lett.* **246**, 70-89.
- Stasiuk, L.D. (1997) The origin of pyrobitumens in Upper Devonian Leduc Formation gas reservoirs, Alberta, Canada: an optical and EDS study of oil to gas transformation. *Mar. Pet. Geol.* **14**, 915-929.
- Worden, R. H. and Smalley, P. C. (1996). H<sub>2</sub>S-producing reactions in deep carbonate gas reservoirs: Kuff Formation, Abu Dhabi. *Chem. Geol.* **133**, 157-171.
- Yue, C. T., Li, S. Y., Ding, K. L. and Zhong, N. N. (2006) Thermodynamics and kinetics of reactions between C<sub>1</sub>-C<sub>3</sub> hydrocarbons calcium sulfate in deep carbonate reservoirs. *Geochem. J.* **40**, 87-94.
- Zhang, S. C., Shuai, Y. H. and Zhu, G. Y. (2008) TSR promotes the formation of oil-cracking gases: Evidence from simulation experiments. *Sci. China, Ser. D: Earth Sci.* **51**, 451-455.
- Zhang, T. W., Ellis, G. S., Wang, K. S., Walters, C. C., Kelemen, S. R., Gillaizeau, B. and Tang, Y. C. (2007) Effect of hydrocarbon type on thermochemical sulfate reduction. *Org. Geochem.* **38**, 897-910.
- Zhang, T. W., Ellis, G. S., Walters, C. C., Kelemen, S. R., Wang, K. S. and Tang, Y. C. (2008a) Geochemical signatures of thermochemical sulfate reduction in controlled hydrous pyrolysis experiments. *Org. Geochem.* **39**, 308-328.
- Zhang T. W., Amrani, A., Ellis, G. S., Ma, Q. S. and Tang, Y. C. (2008b) Experimental investigation on thermochemical sulfate reduction by H<sub>2</sub>S initiation. *Geochim. Cosmochim. Acta* **72**, 3518-3530.