Desulfurization Mechanism of Thioether Compounds in Heavy Oil on the (111) Surface of Inverse Spinel Fe_3O_4

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Fe_3O_4 preparation:

2 mmol of $Fe(NO_3)_3 \bullet 9H_2O$ was dissolved in 50 mL of ethylene glycol under ultrasonic treatment for 20 min to ensure the solid was it fully dissolved completely. Then, pre-configured NaOH solution (6 mol/L) was added to $Fe(NO_3)_3$ solution drop by drop to adjust pH to 9-10. After the solution was stirred evenly, it was transferred to a PTFE liner in a stainless-steel reactor at 180°C for 24 h. After the reaction, the mixture was transferred to a large beaker and washed with distilled water until the upper clear liquid was neutral. Furthermore, the precipitation (Fe_3O_4) was separated and dried overnight under vacuum. Finally, the sample was ground for use.

Figure S1

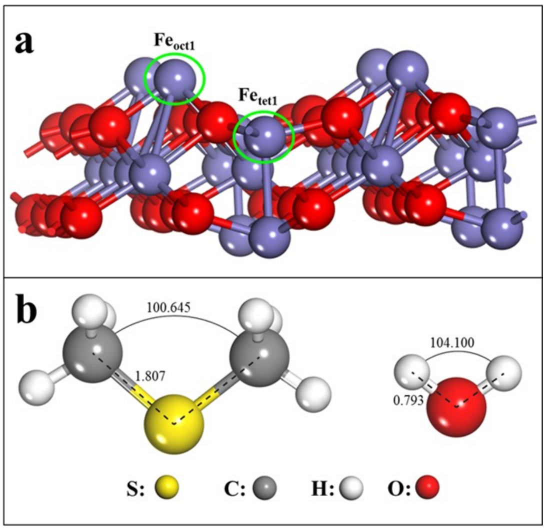

Figure S1 Structure of optimized Fe_3O_4 unit cell, dimethyl sulfide and water molecule models

Figure S2

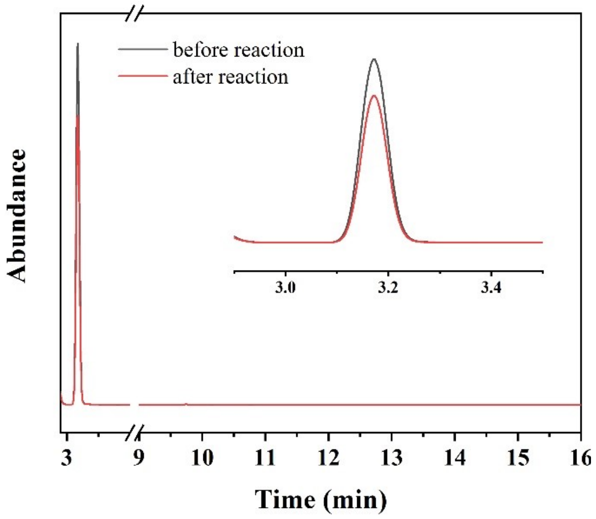

Figure S2 GC-MS spectra of reaction system before and after catalytic reaction; inset shows the amplification of $C_2H_6SC_2H_6$ species.

Referring to the rate-determining step of C-S bond decomposition in thioethers, we simulated the first step of C-S bond dissociation in C_4H_8S and C_4H_4S to compare the catalytic mechanism of different S-containing compounds during aquathermolysis, of which the calculated results were illustrated in **Figure S3** and **Figure S4** Under attack of free H_2O, C-S bond length in C_4H_8S was enlarged to 1.857 Å from 1.837 Å, meanwhile, the O-H in H_2O was extended to 0.982 Å. As the reaction advanced, C-S bond and O-H bond were destroyed, producing final HSC_4H_8OH with S atom and O atom anchored to two nearby Fe atoms. The reaction barrier was 0.779 eV, higher than that of CH_3SCH_3, which should be mainly resulted from the interspace resistance caused by its cyclic structure. Simultaneously, the reaction energy was 0.203 eV indicating an endothermic reaction, high than that of CH_3SCH_3, which should also be relevant to the interspace resistance of the molecule.

Analogously, with respect to C_4H_8S, the existence of H_2O also enlarged the length of C-S bond (1.714 Å→1.736 Å), meanwhile, the O-H bond was extended to 0.977 Å. As the reaction advanced, C-S bond and O-H bond were broken down, with the S atom and O atom in the final HSC_4H_4OH product absorbed to two contiguous Fe atoms. The corresponding activate energy and reaction heat were 1.995 eV and 0.584 eV, higher than C_4H_8S and CH_3SCH_3, which was not only because of the ring structure but the conjugated electrons in the molecule. Herein, the dissociation activity of different S-containing compound followed the trend of straight-chain saturated thioethers > thiophanes > thiophenes could be concluded.

Figure S3

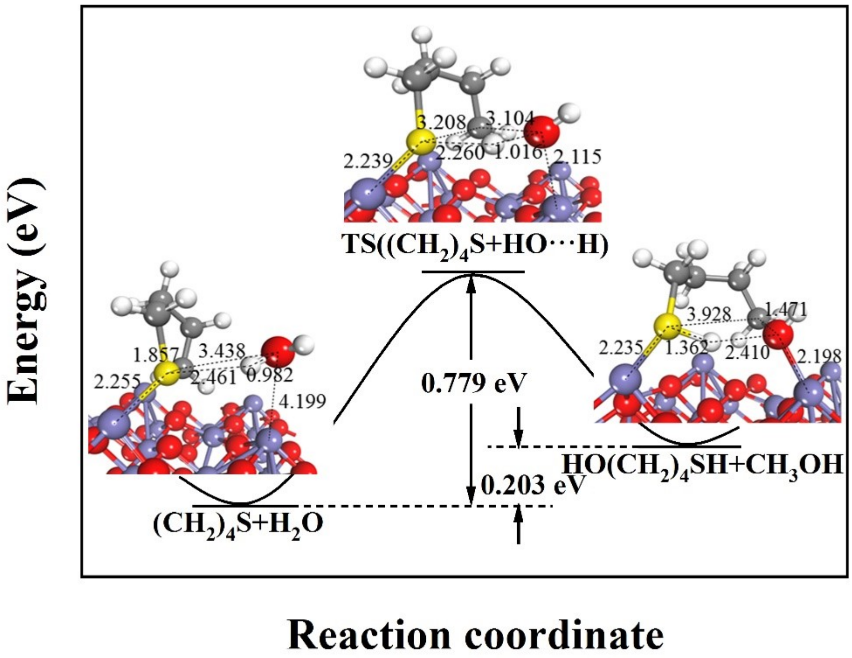

Figure S3 The structure and energy variety of optimized Fe_3O_4 (111) and C_4H_8S during catalytic reaction with assistance of free H_2O molecule

Figure S4

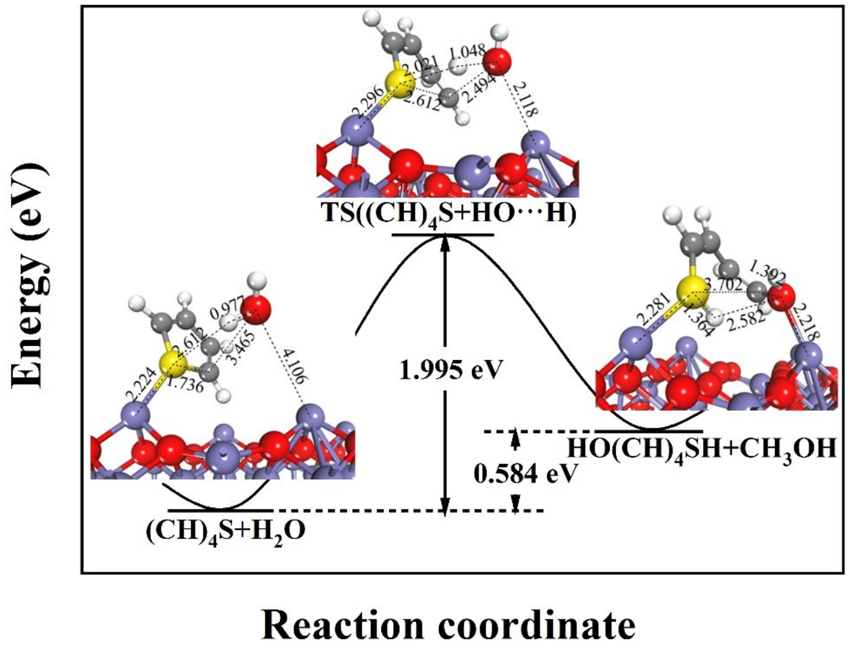

Figure S4 The structure and energy variety of optimized Fe_3O_4 (111) and C_4H_4S during catalytic reaction with assistance of free H_2O molecule

According to optimized catalytic test condition (30% H_2O, 200°C/12 h), the decomposition results of C_4H_8SH, C_4H_8S, C_4H_4S were illustrated in **Figure S5**. After reaction, the decrease of C_4H_8SH and C_4H_8S model was 39.38%, 9.92%, while, the corresponding conversion was 90.86% and 99.22%, which demonstrated the reduced model molecules were almost completely decomposed, indicating a catalytic reduction efficiency matched the regulation of C_4H_8SH> $C_2H_6SC_2H_6$>C_4H_8S. With respect to C_4H_4S, the removal rate was 9.77%, which was parallel with that of C_4H_8S, however, only 10.08% of the eliminated molecules was transformed to small ones, leaving 89.92% of complicated large S-containing compounds. Such a result indicated that C_4H_4S was much more difficult to be dissociated than C_4H_8S, which was coincident with the above theorical conclusion. As a result, thiophene-structure molecules should be the most stable S-containing compounds. For this reason, it could be envisioned that removal of thiophene compounds was hard in aquathermolysis. Consequently, hydrogen donors usually were employed to promote the conversion of thiophenes to thiophanes, leading to an enhanced viscosity reduction during heavy oil catalytic aquathermolysis[1-2]

Figure S5

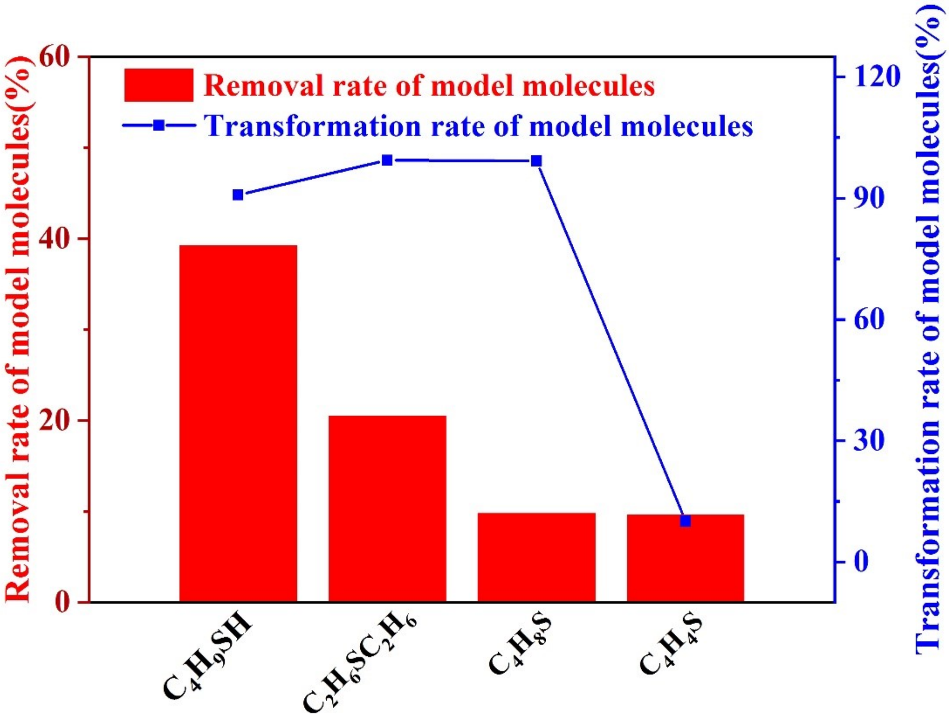

Figure S5 Removal rate and transformation rate of C_4H_9SH, $C_2H_6SC_2H_6$, C_4H_8S, C_4H_4S under equal reaction condition (30% H_2O, 200°C/12 h)

1. Hart, A.; Lewis, C.; White, T.; Greaves, M.; Wood, J., Effect of cyclohexane as hydrogen-donor in ultradispersed catalytic upgrading of heavy oil. *Fuel Processing Technology* **2015,** *138*, 724-733.

2. Yusuf, A.; Al-Hajri, R. S.; Al-Waheibi, Y. M.; Jibril, B. Y., In-situ upgrading of Omani heavy oil with catalyst and hydrogen donor. *Journal of Analytical and Applied Pyrolysis* **2016,** *121*, 102-112.