

Comparison study of sulfur and TSR impact on the gases and carbon isotopic composition of crude oil cracking

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Aiming to assess the effects of sulfur and TSR on the crude oil cracking reaction, a series of the sealed gold tube pyrolysis experiments were performed on a virtually no sulfur crude oil from the Tarim Basin and its combinations with addition of 1% and 5% elemental sulfur, and of CaSO₄ plus water, respectively, under the programmed temperature from 380 to 550°C with a heating rate of 2°C/h. The comparison of results show that: 1) the sulfur impact on the yields of methane depends on the sulfur content, a lower sulfur content (1%) could significantly reduce the methane formation while a higher sulfur content would slightly promote methane generation at the low temperature range and restrain methane yields at higher temperature range; correspondingly, the addition of sulfur has obviously restrained the formation of heavier gases of C₂ to C₅ regardless with the sulfur content; 2) the pyrolyses of crude oil, CaSO₄ and H₂O combination suggest that the existence of H₂O is essential for initiating the TSR reaction while the reaction extent, gas yields and carbon isotopic fractionation seem to be largely controlled by the amount of water involved; 3) the addition of sulfur would generally cause an 2-3‰ of carbon isotopic composition excursion of methane; while the TSR reaction could cause as much as 7‰ carbon isotopic fractionation; 4) In general, the TSR reaction shows remarkable effect on the gases yields and δ¹³C composition compared to that of sulfur. Finally, the effects of sulfur and TSR on the yields of hydrocarbon gases as well as CO₂ and H₂S of oil cracking and their geological implications have been also discussed.

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The vapor pressures of dicarboxylic acids reconsidered: The physical state of the aerosol

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Dicarboxylic acids are common water soluble organic components of atmospheric aerosols. To understand their partitioning between gas and particle phase requires the knowledge of their vapor pressures. Various methods exist for the measurement of vapor pressures of very low-volatility compounds: experimental methods e.g. Knudsen cell effusion, Tandem Differential Mobility Analysis (TDMA), single droplet evaporation observed via light scattering, temperature programmed desorption (TPD) and computational methods e.g. UNIFAC or SPARC. Recently, Bilde *et al.* [1] used a TDMA technique to measure the vapor pressures of the C₃ to C₉ dicarboxylic acids and found their vapor pressures to alternate strongly with the parity of the carbon atoms, with the odd acids exhibiting up to one order of magnitude higher vapor pressures compared to those of the even acids with comparable chain length.

Using single levitated aerosol particles and Mie resonance spectroscopy [2] we investigated evaporation rates of C₂ to C₅ dicarboxylic acid particles in different physical states, namely as a solid, as a saturated aqueous solution and as a supercooled melt. If the solubility and activity of the saturated solution is known the vapor pressure of the solid can be calculated from the supercooled melt data. We found that the vapor pressures of the supercooled melt are about one order of magnitude higher than those of the solids and the saturated solutions, which agree with each other within experimental error. Also, our data agree with those of Bilde *et al.* [2003] within experimental error, if we assume that the odd acids did not effloresce in their experimental setup, while the even acids did. This interpretation is also consistent with the measured effluorescence relative humidities of the dicarboxylic acids. Thus, we conclude that there is no significant even-odd alternation of the vapor pressures of dicarboxylic acids in totally liquid or totally solid aerosol particle and it is important to consider the physical state of the aerosol.

[1] Bilde *et al.* (2003) *Environ. Sci. Technol.*, **37**, 1371-1378.

[2] Zardini *et al.* (2006) *Opt. Express*, **14**, 6951-6962.