

Effects of water on the thermal stability of hydrocarbons and the composition and isotope characteristics of the gas products

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As ubiquitous inorganic agent in subsurface, water can react with hydrocarbons [1], although no consistent opinion about the effects of water on the stability of hydrocarbons were achieved^[2].

In this paper, a series of isothermal gold-tube pyrolysis experiments using *n*-C₁₆ and a marine oil were conducted to study the effects of water chemistry on gas yields and isotopes. It was revealed that the interaction between water and hydrocarbons lead to a relative high content of inorganic gas products. Water showed distinct effect on the cracking of hydrocarbons at lower and higher temperature. Meanwhile, the pH and dissolved salts type and concentration can affect the reaction rate of the organic-inorganic interactions.

The ¹³C of hydrocarbon gas, especially for CH₄ and C₂H₆, was depleted in the presence of water. An enrichment of D for CH₄ and C₃H₈ can be evidently observed in hydrous pyrolysis using H₂O and *n*-C₁₆, whereas, a reverse phenomenon occur for C₂H₆. The increase of δD for all the hydrocarbon gases with the presence of D₂O demonstrates that water has provided hydrogen for generation of hydrocarbon gas in pyrolysis. In addition, the presence of smectite and calcite carbonate can remarkably promote the gas yields. The unique surface acid of clay mineral accelerated the decomposition of D₂O and the exchange of D between water and hydrocarbon gases, though its catalytic effect on generation of gas yields was weaker than the carbonate.

[1] Seewald (2003) *Nature* **426**, 327-333. [2] Lewan (1997) *GCA* **61**, 3691-3723.

Interaction of synthetic manganite with antimony(III)

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Manganese oxides play an important role in many redox processes in the environment, such as oxidation of antimony (Sb) [1]. The kinetics of antimony transformation by synthetic manganite is examined in this study.

The kinetic experiment was carried out with a background electrolyte of 0.01 M NaNO₃ and 5 mM CH₃COONa at pH 4. Sb species were measured by hydride generation atomic fluorescence spectrometer (HG-AFS) (AFS 230, Haiguang Corp., Beijing).

The oxidation of Sb(III) by synthetic manganite is shown in Figure 1. Rapid uptake of Sb(III) by manganite is apparent as well as formation of Sb(V) at the initial period. Then, the Sb(V) in the solution is adsorbed by manganite and reduced gradually with the reaction time. Figure 2 shows the normalized Sb L-edge XANES spectra of reference materials (KSb(OH)₆ and Sb₂O₃) and the samples collected from the Sb(III)-manganite system. It is obvious from the spectra that the absorption edge of Sb(III) shift to higher energy at the Sb(V). This indicates that the adsorbed Sb species on the manganite surface is Sb(V).

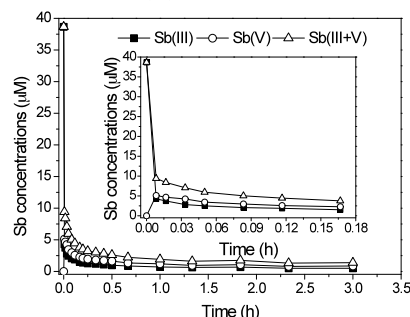


Figure 1: Speciation of dissolved Sb_{total}, Sb(III) and Sb(V) recovery during the reaction of 38.66 µM Sb(III) with synthetic manganite (0.12 g/L) as a function of time at pH 4.0.

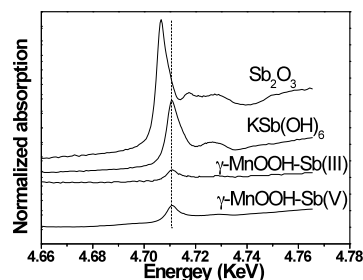


Figure 2: Normalized Sb L-edge XANES spectra

[1]Belzile *et al.* (2001) *Chem. Geol.* **174**, 379-387.