

Desulfurization of Thiophene in Alkaline Supercritical Water Studied by ^1H and ^{13}C NMR

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Thiophene, which is one of the major sulfur-containing compounds in crude oil as well as dibenzothiophene, was successfully desulfurized by the heterolytic cleavage of the C–S–C bond through the treatment with NaOH in supercritical water at 400 °C. Thiophene was disintegrated into S^{2-} and such carboxylic acids as formic, acetic, and succinic acids within 1 h.

Recently, super- and subcritical water has received much attention as an alternative to hazardous organic solvents for a variety of chemical processes.^{1–11} In supercritical water, a number of organic compounds can be decomposed to CO_2 and H_2O or transformed into some others.^{3–11} Complete oxidation in super- or subcritical water has been considered as a remarkable method for the disposal of organic wastes. Used organic compounds are originally synthesized from such fossil fuels as petroleum and coal generated after a geologically long period, and they are still organic resources, as long as the C–C and C–H bonds are retained there. Instead of their burning or complete oxidation in a very short time compared to the geological one, we should develop a new method for converting them into useful organic compounds by finding supercritical water reduction reactions.^{8–11} Chemical recycles using hot water that is friendly to the earth can be effective means of alleviating the resource shortage in the future. For example, upgrading of crude oil is one of the beneficial applications of this method. Crude oil contains sulfur as thiophene and dibenzothiophene that cause SO_x during combustion. Thus it is of great interest to develop the supercritical water cracking of thiophene as in the case of rubber.⁸ To the knowledge of the authors, there has been no report on the desulfurization of thiophene in contrast to dibenzothiophene.^{12–14}

Autoclave used here was made of Hastelloy “C-276” as in a previous study.⁸ The reaction vessel was rolled up and down with a rocking motion of the heater. Such reagents as thiophene, NaOH, and iron powder (300 mesh) were supplied by Wako Chemical Co., Ltd. We poured 0.01 mol of thiophene (the final solution concentration being 0.5 mol/dm³ at ambient conditions) into 20 cm³ of aqueous NaOH solutions at different concentrations in the vessel (inner volume, 45 cm³), and replaced the air in the autoclave with Ar. The reaction mixture was heated up to 400 °C at the rate of 50 °C/min with the induction heater. At each reaction time, the autoclave was cooled down in a few minutes with an electric fan to a temperature required for effective stopping of the reaction. To make the new reaction controllable, we need to identify the sulfur state and organic products by chemical analyses. Before the product analysis, oxidized iron precipitates were removed by filtration. A gaseous product, CO_2 was detected using FT-IR (WINSPEC-50, JEOL). The concentration of the only sulfur product, sulfide ion S^{2-} in the aqueous phase was determined by using methylene blue colorimetry

(as JIS K0101). The organic products in both the aqueous and organic phases were characterized using ^1H and ^{13}C NMR spectroscopy (EX 270 Wide Bore, JEOL). The organic phase consisted only of the remaining reactant with negligible organic products.

First we examined how the desulfurization yield depended on NaOH concentration. The decomposition yield in 20 min at 400 °C was 6.0, 33, 50, 58, and 57% at the NaOH concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 mol/dm³, respectively. Thus the desulfurization becomes efficient when NaOH is added in excess of thiophene. When the concentration is larger than 3 mol/dm³, the efficiency gets almost saturated. Hence we examined the reaction at 3 mol/dm³ of NaOH.

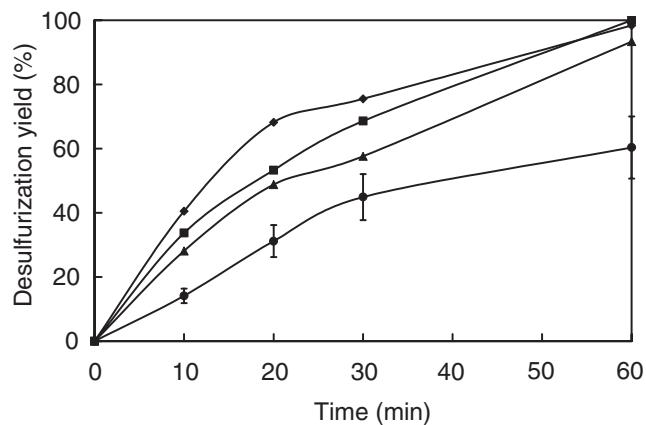


Figure 1. Time dependence of the desulfurization yield at different amounts of Fe; 0 mol (●), 0.01 mol (▲), 0.05 mol (■), and 0.1 mol (◆).

Figure 1 illustrates how the desulfurization yield determined by monitoring S^{2-} varies with time in the presence of Fe. The initial increase of the yield is relatively large up to 20–30 min and after that the increasing rate slightly decreases. The fragmentation reaction is catalyzed by Fe besides NaOH. However, the reaction appears to proceed without Fe. In this case, the yield is limited to 60% in 1 h. This suggests that the reaction is catalyzed by the metal surface of the autoclave. In the gas phase, CO_2 and a small amount of gaseous thiophene were identified by FT-IR depending on the yield. Figures 2a and 2b illustrate the ^1H and ^{13}C NMR spectra, respectively. In Figure 2a, the peaks at 1.9, 2.4, and 8.4 ppm are assigned to the CH_3 of the acetate ion, the CH_2 of the succinate, and the CH of the formate, respectively; cf., the chemical shifts of the CHs in thiophene are 7.1 and 7.3 ppm. Figure 2b shows the carboxyl groups, and that the signals at 169, 182, and 183 ppm are assigned to the carbon-

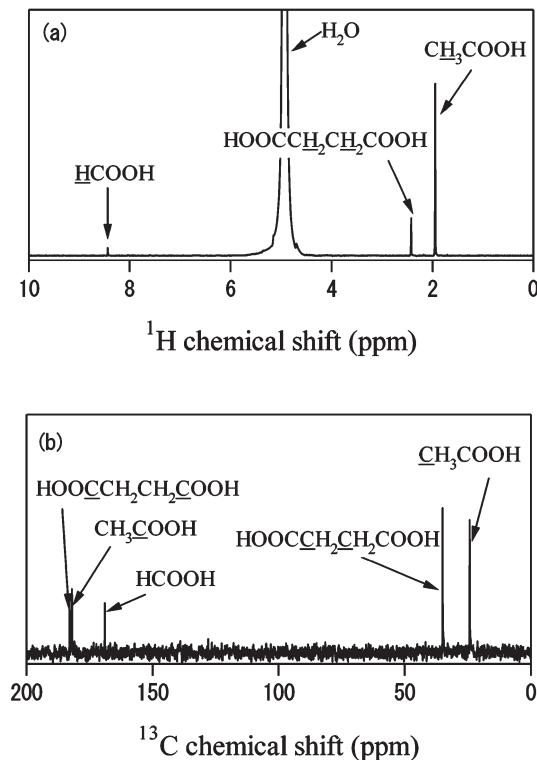


Figure 2. ^1H (a) and ^{13}C NMR (b) spectra of the aqueous phase treated at 400°C for 30 min with $1\text{ mol}/\text{dm}^3$ of NaOH (no Fe added). Free induction decay signals for ^1H and ^{13}C were accumulated for 8 and 15000 times, respectively.

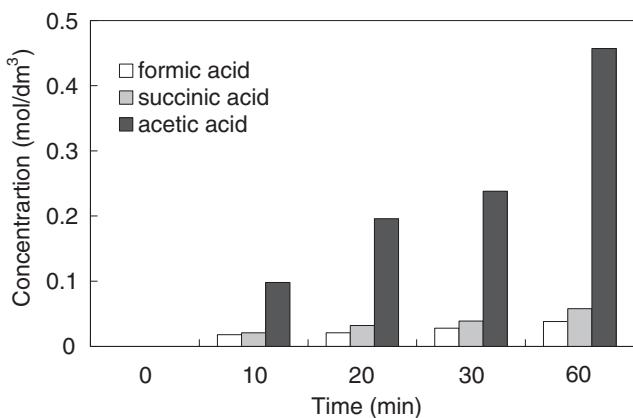


Figure 3. Time dependence of the acids formed from thiophene without Fe in alkaline ($3\text{ mol}/\text{dm}^3$ NaOH) supercritical water at 400°C .

ys of the formate, acetate, and succinate ions, respectively. The ^{13}C peaks at 24 and 35 ppm are assigned to the CH_3 and CH_2

groups for the acetate and succinate, respectively. All of these assignments were confirmed on the basis of the ^1H and ^{13}C NMR spectra taken for the authentic compounds. Hence, it is suggested that the thiophene ring is disintegrated into the three carboxylic acids, formic acid, acetic acid, and succinic acid through the supercritical water desulfurization with NaOH. It is speculated that the reactions proceed via ionic mechanisms due to the presence of NaOH. As mentioned above, CO_2 is observed in the gas phase, and this is due to the decarboxylation of these acids. Figure 3 depicts the product distribution as a function of time. The concentrations of the acid salts were calculated from the peak intensities of the ^1H NMR spectra taken in the aqueous phase. As can be seen, the main product is the acetate, and the total amount of the produced acids is somehow less than that expected from the reaction yield by S^{2-} . The loss is associated with the acid decarboxylation referred to above. It is not yet understood how these carboxylic acids containing 1, 2, and 4 carbons are produced by the alkaline supercritical water desulfurization.

In conclusion, thiophene is completely broken down into three carboxylic acids, liberating S^{2-} in supercritical water within 1 h. Since the carboxylic acids (especially acetic acid) are useful for generating hydrogen, methane, and ethane, the supercritical water reaction studied here can enrich green chemistry.

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