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Enhanced Oxidation of Alkali Metal Acetate in Supercritical Water

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Supercritical water oxidation is an innovative technology for wastewater treatment. Alkali metal acetate could be oxidized in supercritical water at greatly higher rate than that of acetic acid, which is a typical refractory intermediate in organic compound oxidation. Although heterogeneous oxidation catalyzed by in situ formed alkali metal titanate contributed into higher conversion rate, homogenous oxidation in supercritical phase was the main reaction pathway. Enhanced oxidation of alkali metal acetate has great potential to enable short and complete oxidations of refractory organic compounds.

Water above its critical point ($T_c = 374\,°C$, $P_c = 22.1\,MPa$), known as supercritical water, has unique properties that make it homogeneously miscible with organic compounds as well as with oxygen. Therefore, supercritical water serves as an excellent reaction medium for the oxidation of organic compounds without interphase mass-transfer limitations. The oxidation in supercritical water (SCWO) has received a great deal of attention as an innovative and effective treatment process of hazardous organic compounds.[1–4] In conventional SCWO technologies, operational temperature would be up to nearly 500 to 700 °C in order to ensure complete decomposition of refractory by-products like acetic acid and ammonia.[5–7] Therefore, acetic acid has been used as a refractory model compound, and SCWO of acetic acid with/without catalysts has been well reported by many researchers.[6,8,9] If wastewater has acidic or alkaline pH, it should be neutralized before and/or during SCWO treatment in order to prevent reactor corrosion. Although the neutralization would yield organic salts, SCWO of organic salts has been uncertain. Therefore, the objective of this study is to investigate SCWO of organic salts. In this study, acetate salts (alkali metal acetate (Li, Na, and K) and magnesium acetate) were tested as model compounds.

Experimental apparatus consisted of high-pressure pumps (NP-CX: Nihon Seimitsu Kagaku Inc., Japan), preheating lines, a reactor, a type-K thermocouple (T-35: Sakaguchi Dennetsu Inc., Japan), a heat exchanger, a backpressure regulator (44-1100: Tescom Inc., USA), and a gas–liquid separator. An isothermal, isobaric plug flow reactor fabricated from titanium tube (2.10-mm inner diameter, 5–500-cm length, internal volume of 0.175–17.5 mL) was used in all SCWO experiments. Acetic acid and acetate salts (lithium acetate, sodium acetate, potassium acetate, and magnesium acetate) utilized in this paper were analytical grade (Wako Inc., Japan, purity of each reagent >99%). Hydrogen peroxide (30 wt %, Wako Inc., Japan) was used as a source of oxygen through its complete decomposition to oxygen and water during preheating. Pure water was degassed with nitrogen gas before use. Acetic acid/acetate salt solution and hydrogen peroxide solution were fed separately into the reactor at 25 MPa and heated to 450 °C in the preheating line. Fed solutions were mixed before the reactor and passed through it at residence time of 0.32 to 65 s. After the effluent was cooled and depressurized, liquid and gas samples were collected at the sampling port using a glass container and a gas bag, respectively. Concentrations of unreacted acetic acid/acetate salts and intermediates in the effluent liquid samples were analyzed by ion chromatography (IC-500: Shimadzu Inc., Japan) and high-performance liquid chromatography (HPLC, HP series1100: Hewlett-Packard Inc., USA). Total organic carbon (TOC) concentration was measured by a TOC analyzer (TOC-500: Shimadzu Inc., Japan).

Conversions of acetic acid and acetate salts as a function of residence time are shown in Figure 1. Initial concentrations of acetic acid/acetate salts and oxygen under supercritical condition are 9.54×10^{-5} and $1.91 \times 10^{-3}\,mol\,L^{-1}$, respectively. Figure 1 clearly indicates that alkali metal acetate (lithium, sodium, and potassium acetate) was oxidized greatly faster than acetic acid. Conversion of acetate salts excluding magnesium acetate reached to 1.0 within 6.0 s. In addition, the rate of TOC conversion was always almost the same as the rate of acetate salt disappearance. No methane, a trace amount of CO (less than 1%), and the dominant proportion of CO_2 (more than 99%) were detected in gas phase in all measurement cases. This suggests complete oxidation of alkali metal acetate to carbon dioxide,

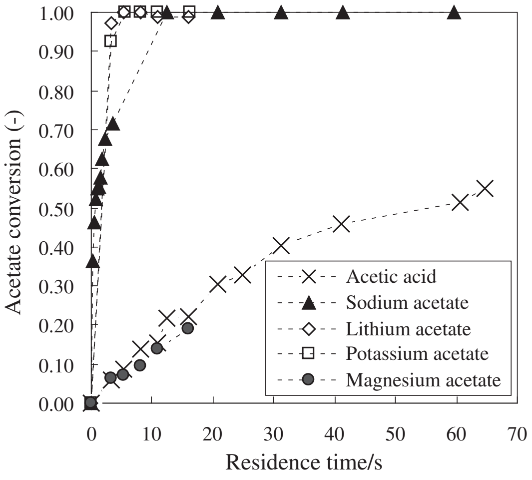

Figure 1. Conversion of acetic acid (×), sodium acetate (▲), lithium acetate (◇), potassium acetate (□), and magnesium acetate (●) at 25 MPa, 450 °C, $9.54 \times 10^{-5}\,mol\,L^{-1}$ of acetic acid/acetate salt feed concentration, and $1.91 \times 10^{-3}\,mol\,L^{-1}$ of oxygen feed concentration.

water, and alkali metal hydroxide. Although formic acid was detected as an intermediate in the effluent, its concentration was always less than the lower limit of quantification (= 3.91×10^{-7} mol L^{-1} in supercritical phase). Carbon mass balances were always within $100 \pm 20\%$ in most cases of sodium acetate oxidation. However, they were only 60–85% when initial feed concentration of sodium acetate was 9.54×10^{-5} mol L^{-1} under supercritical condition. In contrast, there were large unbalances between alkali metal mass input and the output. Lithium, sodium, and potassium mass outputs were 46–99%, 71–78%, and 62–84% smaller than their mass input, respectively. Although residual alkali metals in the reactor could be recovered by pure water cleaning under ambient condition, 34% of fed lithium, 62% of supplied sodium, and 58% of added potassium remained in the reactor. Residual alkali metals will be discussed later. On the other hand, the oxidation rate of magnesium acetate was greatly lower than that of alkali metal acetate and almost the same as that of acetic acid. Insignificant differences between TOC conversions and acetate conversions and dominant proportion of CO_2 in gas phase indicate complete oxidation of magnesium acetate to carbon dioxide, water, and magnesium hydroxide. Only formic acid was detected in the effluent at lower concentration than quantification limit. 99% of added magnesium remained in the reactor under supercritical condition, and 71% still remained after pure water cleaning under ambient conditions.

Conversions of sodium acetate at different oxygen feed concentrations are shown in Figure 2. Oxygen feed concentration ranged from 9.54×10^{-4} to 1.91×10^{-2} mol L^{-1} in supercritical phase, and sodium acetate feed concentration was constant at 9.54×10^{-5} mol L^{-1}. Therefore, molar ratio of oxygen to sodium acetate ranged from 10 to 200. When molar ratio was equal to or more than 20, conversion rate of sodium acetate had no significant differences. Negligible effect of oxygen on conversion rate has been also reported in catalyzed/uncatalyzed acetic acid SCWO[8,9] when molar ratio of oxygen to acetic acid was higher than certain levels. In contrast, significantly negative effect of sodium acetate feed concentration on conversion rate appeared even under oxygen-rich condition, in which molar ratio was 20. Conversions of sodium acetate at different sodium acetate feed concentrations are shown in Figure 3. Oxygen feed concentration was constant at 1.91×10^{-2} mol L^{-1}, and sodium acetate feed concentration ranged from 9.54×10^{-5} to 9.54×10^{-4} mol L^{-1} in supercritical phase. Conversion at residence time of 1.56 s decreased from 0.57 to 0.28 with the increase of sodium acetate feed concentration.

This negative effect of sodium acetate feed concentration on acetate conversion suggested two possible mechanisms of sodium acetate oxidation. The first is the hydrolysis of sodium acetate to acetic acid and sodium hydroxide. If higher feed concentration of sodium acetate promoted the hydrolysis to acetic acid, it would cause lower global oxidation rate because conversion rate of acetic acid is greatly lower than that of sodium acetate, as shown in Figure 1. The calculation using ionization equilibrium constants of sodium acetate,[10] acetic acid,[11] and sodium hydroxide[12] under supercritical conditions suggested that only 0.06–0.45% of fed sodium acetate were hydrolyzed to acetic acid and that 41–77% were ionized as acetate anion under tested conditions. Therefore, the hydrolysis to acetic acid could not explain the negative effect of sodium acetate feed concentration on conversion rate. On the other hand, this calculation implied the importance of acetate anion oxidation on oxidation mechanism of sodium acetate in supercritical phase.

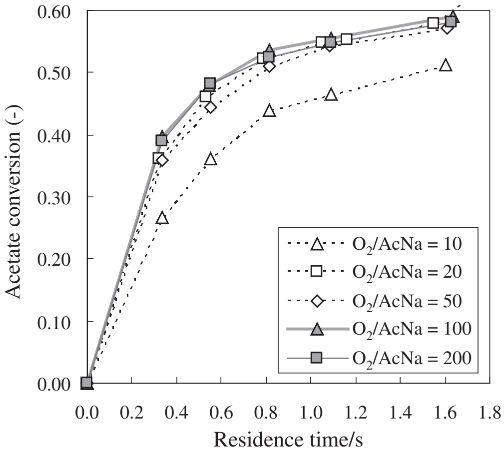

Figure 2. Effect of oxygen feed concentration on sodium acetate conversion at 25 MPa, 450 °C, and 9.54×10^{-5} mol L^{-1} of sodium acetate feed concentration (Molar ratio of oxygen to sodium acetate: 10 (△), 20 (□), 50 (◇), 100 (▲), and 200 (■)).

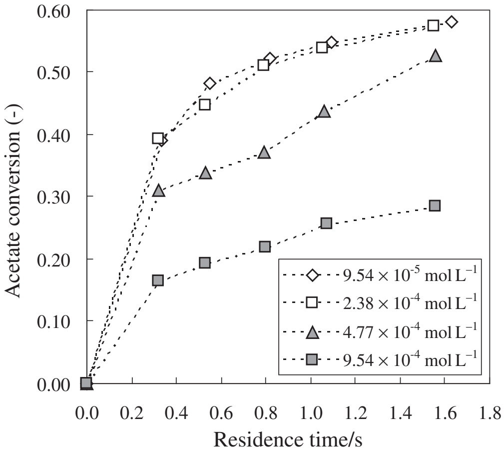

Figure 3. Effect of sodium acetate feed concentration on sodium acetate conversion at 25 MPa, 450 °C, and 1.91×10^{-2} mol L^{-1} of oxygen feed concentration (Sodium acetate feed concentration: 9.54×10^{-5} (◇), 2.38×10^{-4} (□), 4.77×10^{-4} (▲), and 9.54×10^{-4} mol L^{-1} (■)).

The other suggested mechanism is parallel reaction pathways consisting of minor homogeneous oxidation in supercritical phase and major heterogeneous oxidation on reactor surface. In this case, adsorption of oxygen and/or sodium acetate to reactor surface or reactions of adsorbed oxygen/sodium acetate (Langmuir–Hinshelwood or Eley–Rideal mechanism) are assumed as the rate-limiting step. Global oxidation rate would decrease when feed rate of sodium acetate exceeds heterogeneous oxidation rate on reactor surface. Hydrothermal synthesis of titanate minerals on the surface of titanium reactor likely played an important role in heterogeneous oxidation. Takahashi et al.[9] reported hydrothermal synthesis of sodium titanate in supercritical water using sodium carbonate and its

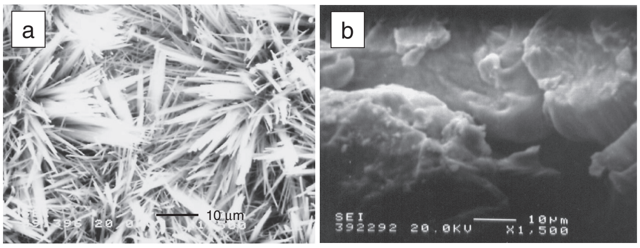

Figure 4. SEM photographs of sodium titanate (a) and magnesium titanate (b).

great catalytic effect on SCWO of acetic acid. Alkali metal hydroxide and magnesium hydroxide, which were produced from the decomposition of acetate salt, might react with titanium on reactor surface and generate titanate minerals during acetate salt oxidation. In addition, they might also have catalytic effect on acetate salt oxidation. As is expected, sodium titanate, potassium titanate, and magnesium titanate were synthesized on titanium reactor surface during acetate salt oxidation experiments. They could be observed by scanning electron microscope–energy dispersive spectroscopy (SEM–EDS). SEM photographs of sodium titanate and magnesium titanate are shown in Figure 4. Hydrothermal synthesis of sodium, potassium, and magnesium titanate explained residual sodium/potassium/magnesium in the reactor after pure water cleaning. However, obvious synthesis of lithium titanate could not be observed even though 34% of fed lithium still stayed in the reactor after pure water cleaning. Titanate minerals synthesized through acetate salt oxidation also had a catalytic effect on acetic acid oxidation. The results of acetic acid oxidation using a fresh titanium reactor or modified reactors, in which titanate minerals were synthesized on the surface through acetate salt oxidation, are shown in Figure 5. The reactor modified with sodium titanate generated higher conversion rate of acetic acid than the fresh reactor and other modified reactors did. In the case of sodium titanate-modified reactor, heterogeneous oxidation of acetic acid, which was catalyzed by sodium titanate, promoted 104–260% higher global conversion rate. However, catalytic effect of sodium titanate on sodium acetate oxidation was lower than that on acetic acid oxidation. Compared to the results of sodium acetate oxidation using fresh titanium reactor, sodium acetate oxidation using a reactor modified satisfactory with sodium titanate generated only 1.9–34% higher conversion rate. In the case using a fresh reactor, the reactor was changed to a new one after one data measurement in order to minimize sodium titanate synthesis. This study showed that heterogeneous oxidation, which was catalyzed by sodium titanate synthesized on titanium reactor surface, is one of significant reaction pathways in SCWO of sodium acetate. This was supported by different conversions of sodium acetate when other reactors made of SUS-316 or hastelloy were used. However, homogeneous oxidation, in particular acetate anion oxidation, in supercritical phase is likely the main reaction pathway. Further study is necessary to explain detailed mechanisms of sodium acetate oxidation under supercritical conditions.

Alkali metal acetates were oxidized completely to carbon dioxide at greatly faster conversion rate than that of acetic acid. Enhanced oxidation of alkali metal acetates suggests positive effect of the neutralization to oxidize acidic wastewater by SCWO treatment. This has a great potential to enable short and complete oxidation of organic compounds, in particular refractory organic acid. However, the deposition of inorganic salts, which would be produced from the oxidation of organic acid salts, should be successfully managed to apply this technology to wastewater treatment. Hydrothermal synthesis of titanate minerals during acetate salt oxidation suggests great potential of titanium material as catalyst. On the other hand, it also suggests that non-titanium reactor should be used in a SCWO process to prevent the corrosion.

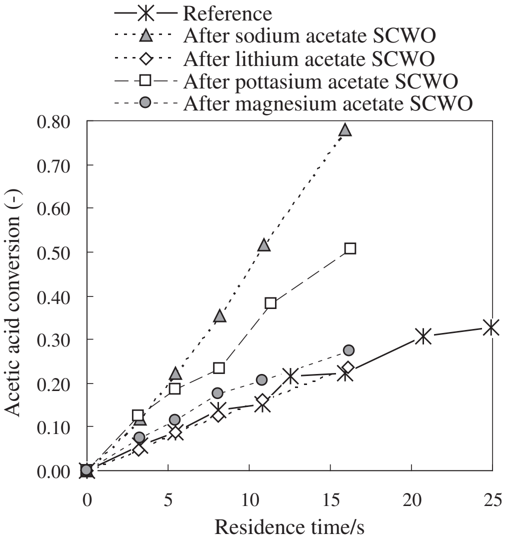

Figure 5. Conversion of acetic acid at 25 MPa, 450 °C, 9.54×10^{-5} mol L^{-1} of acetic acid feed concentration, and 1.91×10^{-3} mol L^{-1} of oxygen feed concentration with a fresh reactor (⚹) or a reactor modified by SCWO of sodium acetate (▲), lithium acetate (◇), potassium acetate (□), or magnesium acetate (●).

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