Supercritical water oxidation process utilizing salts contained in liquid waste as catalyst

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Abstract

Sodium titanate was hydrothermally synthesized during the deposition of sodium hydroxide, sodium carbonate, and sodium acetate on the surface of titanium particles packed in a reactor. It showed a significant catalytic effect on the oxidation of acetic acid and phenol (25 MPa, 450 °C). Titanium particles accelerated the deposition of sodium in the case of sodium hydroxide, sodium carbonate and sodium acetate. It promoted sodium deposition slightly in the case of sodium sulphate and sodium phosphate. In contrast, it showed no influence on sodium deposition in the case of sodium chloride. More than 87% of deposited sodium was recovered from the reactor under sub-critical conditions (25 MPa, 350 °C). A new SCWO process utilizing salts contained in liquid waste as catalyst was proposed based on these results.

Keywords: supercritical water oxidation, wastewater, salt deposition, catalyst.

1 Introduction

The oxidation in supercritical water (SCWO) is attracting a great deal of attention as an innovative and effective treatment process of hazardous organic compounds [1-4]. Owing to the significant drop in the density, dielectric constant and ability to form hydrogen bond that occurs under supercritical conditions of water (Tc>374 °C, Pc>22.1 MPa), supercritical water is an excellent solvent for organic compounds and oxygen. Supercritical water acts as a single-phase medium for rapid and complete oxidation of hazardous organic compounds to carbon dioxide, water, nitrogen gas and inorganic acids. SCWO processes enable complete destruction of organic wastes in a short residence time, much economy
of off-gas treatment comparing incineration, and small reactor volume required. Furthermore, it is noted that the boundary of material management is easy to be taken, in case a process failure happens, because most of toxic residuals, by-products, or intermediates, if any, must be remained in the effluent liquid phase.

For practical application of SCWO to the treatment of wastewater, however, it needs countermeasures against two significant problems. One is severe corrosion of the reactor owing to a high temperature operation. A simple preventive measure against the corrosion is to decrease operational temperature, which could be achieved by utilizing catalysts. Some catalysts showed advantages on the destruction of refractory organic compounds in SCWO [5-9]. Catalytic effect of sodium carbonate (Muthukumaran and Gupta [7]), sodium hydroxide (Lee et al [8]) and sulphate salts of transition metals (Gizir et al [9]) on SCWO of 2-chlorophenol or phenol were interestingly reported. Therefore, it is reasonably expected that some salts or metals contained in wastewater, typically sodium salts, might be served as catalyst on SCWO of hazardous organics. This study especially found the catalytic effect of sodium titanate, which was hydrothermally synthesized on titanium particles packed in a SCWO reactor. Acetic acid and phenol were tested as model organic substances. The other problem is fatal plugging caused by the deposition of inorganic salts contained in wastewater at bottlenecks of the supercritical treatment zone of the process. The salts definitely precipitate there due to low density and dielectric constant of supercritical water. If the wastewater includes salts, its deposition in SCW is inevitable to some extent. Therefore, it is important to know how to control the deposition rather than how to eliminate it. From this viewpoint, it is worthwhile to consider an intended salt deposition and periodical its cleaning in the first part of the reactor that would prevent from a fatal plugging at the following parts. This paper will propose such a process.

2 Experimental

Experimental apparatus consisted of high-pressure pumps (Nihon Seimitsu Kagaku Co), pre-heating lines, a reactor, a thermocouple (Sakaguchi Dennetsu Co), a heat exchanger, a backpressure regulator (Tescom Co) and a gas-liquid separator (Fig. 1). All experiments were conducted in an isothermal, isobaric fixed-bed plug flow reactor fabricated from SUS 316 tubing (7.05 mm ID, 7 cm length, internal volume of 2.73 ml). Acetic acid, sodium acetate, sodium chloride, sodium hydroxide, sodium carbonate, sodium sulphate, sodium phosphate and phenol utilized in this study were analytical grade (Wako Co, purity of each reagent>99%). Hydrogen peroxide (Wako Co, 30 wt%) was used as source of oxygen in SCWO of acetic acid and phenol. Pure water was degassed by nitrogen gas before use. Particles of sponge titanium (Toho titanium Co, purity>98%, φ0.84 to 3.35 mm) were utilized as a catalyst precursor and a salt trapper. All runs were carried out at 25±0.15 MPa, 350±2 or 450±2 °C. Solution of a reagent and water (or hydrogen peroxide solution in SCWO experiments) were fed separately into the reactor in the absence/presence of titanium particles at designed pressure and heated to targeted temperature in pre-
3 Results and discussion

3.1 Catalytic effect by sodium titanate

Spicular crystals were hydrothermal synthesized on the surface of titanium particles packed in the reactor during the deposition of sodium carbonate ([Na₂CO₃]₀ =9.54×10⁻⁵ mol-Na/L (in the reactor)) at 25 MPa, 450 °C. A photograph of the crystals taken by SEM is shown in Figure 2. The composition of the crystals analyzed by SEM-EPMA was oxygen, sodium and titanium. It showed the crystals formed on titanium particles were sodium titanate. Sodium titanate was also synthesized during the deposition of sodium hydroxide and sodium acetate at 25 MPa, 450 °C. Sodium titanate on titanium particles showed significant catalytic effect on the oxidation of acetic acid and phenol at 25 MPa, 450 °C (Fig. 3). Acetic acid and phenol are typical refractory compounds in SCWO. The conversions of acetic acid and phenol were up to 0.85 at the residence time of 7.2 s and 0.73 at 9.3 s, respectively, while their conversions in the absence of sodium titanate were 0.36 and 0.06, respectively. These results
showed a great potential of the use of titanium particles as a catalyst precursor. In real treatment of wastewater by SCWO process, it is reasonably expected that sodium salts contained in wastewater are deposited on titanium particles and then some of deposited sodium react with titanium to form sodium titanate hydrothermally. Sodium titanate synthesized on titanium particles might be served as an effective in-situ catalyst on the oxidation of hazardous organic compounds.

Figure 2: Pictures of sodium titanate synthesized on the surface of titanium particles at 25 MPa, 450 °C (3700 times macro photograph).

Figure 3: Catalytic effect by sodium titanate on the oxidation of acetic acid (a) and phenol (b) at 25 MPa, 450 °C (( a): [CH$_3$COOH]$_0$ =9.54×10$^{-5}$ mol/L (in a reactor); [O$_2$]$_0$ =1.91×10$^{-3}$ mol/L (in a reactor); ( ▲ ) no sodium titanate: (■) existence of sodium titanate), ([b]: [phenol]$_0$ =1.24×10$^{-3}$ mol/L (in a reactor); [O$_2$]$_0$ =8.69×10$^{-3}$ mol/L (in a reactor); (*) no sodium titanate; (Δ) existence of sodium titanate).
3.2 The deposition of sodium salts

With respect to an intended salt deposition, the titanium particles packed in a reactor might play as a salt trapper. In order to know the potential of titanium particles as a salt trapper, the deposition of sodium salts on titanium particles was investigated. Sodium chloride, sodium hydroxide, sodium carbonate, sodium sulphate, sodium phosphate and sodium acetate were tested as model salts. The ratio of deposited sodium to influent sodium (D/I) was calculated by the following equation.

\[
D/I = \frac{C_0 - C_{\text{eff}}}{C_0},
\]

where \(C_0\) and \(C_{\text{eff}}\) are respectively influent and effluent concentration of the reactor. Figure 4 shows D/I values in the case of sodium carbonate when 0 to 3.26 g of titanium particles were packed in the reactor. About 70% of the influent sodium was deposited in the reactor that more than 2.31 g of titanium particles were packed, while it was only 16% without titanium particle. It showed that the titanium particles, if they were enough added, could accelerate the deposition of sodium carbonate. Sodium concentration in the effluent was less than the solubility of sodium carbonate in supercritical water at 25 MPa, 450 °C reported by Khan and Rogak [10] (Fig. 5). This suggests that no more deposition would occur downstream. The reason why the effluent concentration was lower than the solubility might be explained by the continuous consumption of sodium in the bulk by the growth of sodium titanate crystals on the surface. D/I values for the deposition of other sodium salts with and without titanium particles are shown in Table 1. In the case of sodium hydroxide and sodium acetate, D/I value was increased drastically to 0.78 and 0.76, respectively in the presence of titanium particles, while it was as low as in 0.24 and 0.007, respectively, without titanium particles. In contrast, D/I value for the deposition...
of sodium chloride was almost nil regardless of the presence of titanium particles. The negative values of D/I in Table 1 could be regarded as experimental error. In the case of sodium sulphate and sodium phosphate, a little increase in D/I values was observed by the addition of titanium particles. In order to clarify this, however, further experiments at lower concentrations of these salts comparing their solubility are needed.

![Figure 5: Sodium concentration in effluent at 25 MPa, 450 °C (♦) [Na₂CO₃]₀ = 9.54 × 10⁻⁵ mol-Na/L (in a reactor); (∆) [Na₂CO₃]₀ = 1.91 × 10⁻⁴ mol-Na/L (in a reactor); (*) [Na₂CO₃]₀ = 4.72 × 10⁻⁴ mol-Na/L (in a reactor); dashed line: the solubility of sodium carbonate at 25 MPa, 450 °C reported by Khan and Rogak [10].](image)

Figure 5: Sodium concentration in effluent at 25 MPa, 450 °C (♦) [Na₂CO₃]₀ = 9.54 × 10⁻⁵ mol-Na/L (in a reactor); (∆) [Na₂CO₃]₀ = 1.91 × 10⁻⁴ mol-Na/L (in a reactor); (*) [Na₂CO₃]₀ = 4.72 × 10⁻⁴ mol-Na/L (in a reactor); dashed line: the solubility of sodium carbonate at 25 MPa, 450 °C reported by Khan and Rogak [10].

3.3 The recovery of deposited sodium salts from a reactor and the regeneration of titanium particles

Continuous deposition of salts on titanium particles finally causes the plugging. Before the plugging, the removal of deposited salts from a reactor is needed. Water under sub-critical condition (sub-critical water) shows the opposite behaviour in contrast to supercritical water. It shows extremely high ionic product and acts as strong polar solvent, which can easily dissolve inorganic salts. Sub-critical water might be served as an excellent remover of deposited salts. All runs on salt recovery from a reactor under sub-critical condition (25 MPa, 350°C) were conducted utilizing sodium salts described in 3.2 except for sodium acetate. The ratio of recovered sodium from the reactor to the deposited sodium (R/D) was calculated (Table 2). The amount of sub-critical water fed into the reactor was about 150 ml in all runs. More than 87% of deposited sodium was recovered from the reactor in every case. R/D values would increase more if more amounts of sub-critical water were fed into the reactor. Sodium titanate synthesized on titanium particles was hydrolyzed under sub-critical critical condition and the sodium contained in sodium titanate could be recovered from the reactor. This means the titanium particles were regenerated at the same time.
The similar experiment was repeatedly done and the regenerated titanium particles showed the same activity on salt trapping as that of fresh ones. Sodium titanate on regenerated titanium particles also the same catalytic effect comparing that on fresh ones.

Table 1: D/I for the deposition of sodium salts ([salt]₀ = 9.54×10⁻⁵ mol-Na/L (in a reactor) ) in the absence/presence of titanium particles at 25 MPa, 450 °C.

<table>
<thead>
<tr>
<th>Titanium particles</th>
<th>D/I (-)</th>
<th>3.26 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>-0.005</td>
<td>-0.017</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.240</td>
<td>0.782</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>0.159</td>
<td>0.704</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.967</td>
<td>0.995</td>
</tr>
<tr>
<td>Na₃PO₄</td>
<td>0.947</td>
<td>0.952</td>
</tr>
<tr>
<td>CH₃COONa</td>
<td>0.007</td>
<td>0.757</td>
</tr>
</tbody>
</table>

Table 2: Recovery of deposited sodium under sub-critical condition 25 MPa, 350 °C).

<table>
<thead>
<tr>
<th>Salt</th>
<th>R/D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.871</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.888</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>0.904</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.957</td>
</tr>
<tr>
<td>Na₃PO₄</td>
<td>0.997</td>
</tr>
</tbody>
</table>

3.4 Proposed process

A new SCWO process for the treatment of hazardous wastewater that contains toxic organic compounds and inorganic salts could be proposed based on this work. The process flow chart is shown in Figure 6. The operation procedure is described as follows. Wastewater and air as oxidant are fed separately into a reactor. Titanium particles are partially but enough packed in the front part of the reactor and they play two significant roles in this process. One is a salt trapper and the other is a catalyst precursor. Titanium particles as a salt trapper accelerate the deposition of inorganic salts because they significantly increase effective surface area in a small reactor volume. Salts are removed from the bulk and the concentration of salts in the bulk dramatically drops. It enables to prevent from the plugging downstream. Some of deposited salts react with titanium and sodium titanate was hydrothermally synthesized, then they are served as in-situ catalysts that promote the oxidation of hazardous organic compounds. The in-situ catalysts must be active through the treatment because of
their continuous formation and stability in SCW. Feeds of wastewater and air are stopped before the plugging due to excess salt deposition on the titanium particles. Then, treated water is fed into the reactor and operational temperature is decreased a little bit below the critical temperature. Sub-critical condition is kept in the reactor and sub-critical water dissolves the deposited salts and hydrolyzes the in-situ catalysts. Catalysts precursor is regenerated and salts are recovered from the reactor. Some of salts can be added in wastewater as source of catalyst, if necessary. This process might have great advantages for the treatment of wastewater that contains both inorganic salts and hazardous organic compounds because it enables the separation of organic compounds and inorganic salts, the treatment of organic compounds and the recovery of salts at high concentration through the cyclic operation.

Figure 6: Flow chart of designed process ((1a and b) high-pressure pump; (2) pre-heater; (3) a reactor that catalyst precursor packed; (4) heat exchanger; (5) back-pressure regulator; (6) post-treatment of treated water; (7) Reflux flow of treated water into a reactor for the recovery of deposited salts; (8) Flow of water that recovers deposited salts from a reactor; (9) post-treatment of recovered inorganic salts; (10) flow of recycled salts as source of catalyst; (11) flow of post-treated water).

4 Conclusions

Sodium titanate was hydrothermally synthesized on the surface of titanium particles during the deposition of sodium hydroxide, sodium carbonate and sodium acetate. It showed significant catalytic effect on SCWO of acetic acid and phenol. It implies the potential of titanium particles as catalyst precursor and sodium titanate as an in-situ catalyst. Titanium particles as a salt trapper promoted the deposition of sodium in the case of sodium hydroxide, sodium
carbonate and sodium acetate. It also accelerated sodium deposition a little in the case of sodium sulphate and sodium phosphate. In contrast, it showed no influence in the case of sodium chloride. More than 87% of deposited sodium was recovered from a reactor under sub-critical condition. A new SCWO process utilizing salts contained in liquid waste as catalyst was proposed based on these results.

References