Heterogeneous 촉매상에서의 TPA 공정폐수의 CSCWO

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Catalytic supercritical water oxidation of TPA wastewater over heterogeneous catalysts

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Introduction

Supercritical water oxidation (SCWO) is form of hydrothermal treatment. The primary advantage of SCWO process over such land-based alternatives as landfilling, deep-well injection and lagooning is that it is a destruction method. Land-based disposal does not address the ultimate destruction of toxic components of the waste. Each method can result in the possible contamination of surrounding soil and groundwater. Deep-well injection systems are subject to plugging or fouling if organic concentration of 1% or higher are allowed. Landfills and lagoons can contribute to contamination of the air by volatile organics. There is increasing public concern and regulatory action, which will restrict or prohibit land-based disposal of many organic wastes

Wastewater from the TPA manufacturing process (cobalt-manganese-bromine catalyst and acetic acid solvent) is generally the mixture of benzoic acid, 4-formylbenzoic acid, p-tolualdehyde, p-toluic acid, 4-carboxybenzyl alcohol, ethyl benzene, p-toluyl alcohol, benzaldehyde, p-acetoxy-methylbenzoic acid, isophthalic acid, o-toluic acid, p-methylbenzyl acetate, acetophenone, methyl acetate, cobalt acetate, manganese acetate, hydrobromide.

This wastewater is treated by aerobic wastewater treatment, and after sludge has is dried, is incinerated. However, aerobic wastewater treatment requires lots of time, space and flow out process water. Therefore, in this study, SCWO would be introduced to cover disadvantage in the aerobic wastewater treatment.

Experimental

The experiment apparatus was composed mainly of feed pump, wastewater storage, hydrogen peroxide storage, preheater, reactor, heat exchanger, filter, back pressure regulator, G/L separator and so on. This system was designed so that wastewater and hydrogen peroxide do not come in contact

with each other until they have been pressurized and heated to the desired reaction conditions.

Each of the wastewater and the oxygen solution is heated in 1/16-in. OD x 4m length of SS 316 tube coiled in a preheater. The both streams were mixed at the reactor inlet. The reactor was made of stainless steel 316 (280mm long x 18mm OD x 9.5mm ID).

Supercritical water oxidation is influenced by a catalytic effect of the reactor wall. The main components of SUS 316 are Fe, Ni, and Cr, which can be formed transition metal oxide compounds during SCWO. Transition metal oxide compounds can be worked for a role of catalysis during SCWO. Therefore we assumed there is a catalytic effect of the reactor wall in addition to the effect of catalyst at this work.

A commercial catalyst, γ-Al_2O_3 (AL-3992 E, -6+7mesh, 99.9wt%, 190m^2/g, Engelhard) was packed in the reactor. The active ingredients of the $MnO_2/Al_2O_3/CuO$ catalyst (CARULITE 150, -5+6mesh, Carus Chemical) are 45~60% MnO_2 and 1~3% CuO, which are supported on amorphous Al_2O_3. All experiments except for the deactivation studies were conducted using fresh catalyst.

Results and Discussion

Figure 1 shows the conversion as a function of contact time. It is clear that the activity order is $MnO_2/Al_2O_3/CuO$ > γ-Al_2O_3 > Non- catalytic.

The activity of the γ-alumina catalyst did not change significantly during SCWO in 5 hours at a constant process condition (T = 490℃, P = 240bar, contact time = 30sec, $[COD]_0$ = 4.3mmol/L, $[O_2]_0$ = 2.0mmol/L), wastewater conversion was gradually decreased from 0.62 to 0.55. After SCWO of wastewater in 45hours, the structure of γ-alumina pellet was collapsed into powder, only half was remained as its original form. The mechanical strength became deteriorated. The surface area of the catalyst (BET) after SCWO in 45hours was decreased from 190 to 6m^2/g.

Supercritical water oxidation system in this work can be applied to TPA manufacturing system. In Figure 2, it is demonstrated that wastewater can be converted to high quality process water and be recycled. One can get almost 100% conversion at longer contact time, higher temperature or higher concentration of oxygen. If treated wastewater is recycled in TPA manufacturing plant, the recycled water should not have an adverse effect on the product specification of TPA such as purity, color so on.

Table 1 displays comparisons of power rate law kinetic model from SCWO over different heterogeneous catalysts. From the table 1 the activation energy for oxidation of TPA are ordered as follows: Non-catalytic> γ-Al_2O_3 > $MnO_2/Al_2O_3/CuO$. The lowest activation energy was obtained over $MnO_2/Al_2O_3/CuO$ catalyst, which is the evidence of the highly active catalyst for oxidation of TPA.

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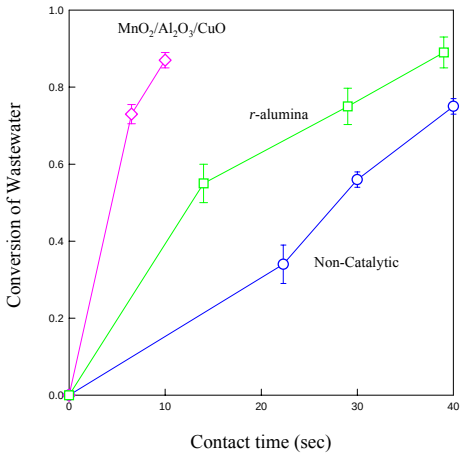

Figure 1. Wastewater conversion from SCWO over different heterogeneous catalysts

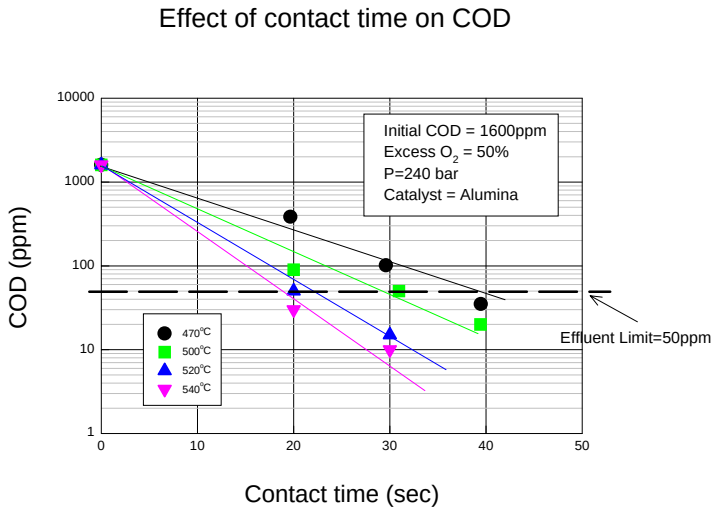

Figure 2. Conditions of high quality process water after SCWO

Table 1. Comparisons of oxidation over different heterogeneous catalysts at supercritical condition

	Non-catalytic	γ- Al_2O_3	$MnO_2/Al_2O_3/CuO$
Range of Temperature (℃)	420~500	420~510	380~440
Range of Pressure (bar)	220~280	220~300	240~320
Oxidant	H_2O_2	O_2	H_2O_2
Rate = $-k[COD]^a[Oxidant]^b[H_2O]^c$	a = 0.65 b = 0.38 c = -0.16	a = 0.81 b = 0.49 c = 0	a = 0.93 b = 0.10 c = -1.00
Activation Energy (kJ/mol)	73.800	55.456	36.587
Method of analysis	Excess method	Least squares and initial rate method	Excess method