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Catalytic oxidation of acetic acid over sodium titanate synthesized hydrothermally in supercritical water

Fumitake Takahashi[a,*], Zhirong Sun[b], Kensuke Fukushi[c], Yoshito Oshima[d], Kazuo Yamamoto[e]

[a] Faculty of Urban and Environmental Engineering, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
[b] School of Environmental and Energy Engineering, Beijing University of Technology Pingleyuan 100, Chaoyang District, Beijing 100022, PR China
[c] Transdisciplinary Initiative for Global Sustainability, the University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[d] Department of Environment Systems, Graduate School of Frontier Sciences, the University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa 277-8563, Japan
[e] Environmental Science Center, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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ABSTRACT

Sodium titanate was hydrothermally synthesized on the surface of titanium particles in supercritical water. Sodium titanate showed catalytic activity on supercritical water oxidation (SCWO) of acetic acid and promoted oxidation rate greatly comparing to uncatalyzed oxidation. Global rate law based on power-law model and Langmuir–Hinshelwood model could describe experimental results well. In addition, Mars–Van Krevelen model expresses catalytic process well. This suggested that redox reaction over sodium titanate might be a dominant oxidation mechanism, at least, above 450 °C. Deactivated sodium titanate was easily re-synthesized and it recovered catalytic activity. Sodium titanate showed a great potential of a long-term available catalyst in SCWO processes through its cyclic re-activation.

1. Introduction

Water above its critical point ($T_c = 374\,^\circ\mathrm{C}$, $P_c = 22.1$ MPa), called 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 550–650 °C in order to ensure complete decomposition of toxic by-products [5]. Such high-temperature operation, however, adversely poses salt precipitation problems due to its low solubility in supercritical water and possibly less processing cost-efficiency. Mineral salts contained in wastewater and resulting from the neutralization of inorganic acids, which are produced from hetero atoms in organic compounds, would settle out at supercritical zone, especially its bottlenecks. Lower temperature and consequently higher water density during SCWO treatment are preferable to mitigate salt deposition issues and potentially to reduce the processing cost [6] because salts are much more soluble in the bulk at lower temperature. As potential means of decreasing the operational temperature, catalytic SCWO has been motivated [7].

Catalytic SCWO can be said as an extended technology of catalytic wet air oxidation, which has been reviewed by Matatov-Meytal and Sheintuch [8]. In the field of catalytic SCWO, which has been reviewed by Ding et al. [7], the oxidative destruction of many organic compounds has been tested as well as catalyst activity and stability in SCW. For example, higher conversion of 2-chlorophenol over sodium hydroxide [9] and transition metal sulphates ($CuSO_4$, VSO_4, $FeSO_4$, $MnSO_4$, $NiSO_4$ and $CoSO_4$) [10] as homogeneous catalyst was reported. In cases of heterogeneous catalysts, phenol over MnO_2 [11,12], V_2O_5, Cr_2O_3 [13], CuO/ZnO [14], Cu/Zn/Co oxides [15] as metal oxide catalyst and over activated carbon as nonmetallic catalyst [16] have been investigated. Acetic acid is frequently used as model compounds as well as phenol due to its relatively strong resistance in SCWO. Catalytic activities on the oxidation of acetic acid over MnO_2/CeO_2 [17], TiO_2 [18], $CuO/ZnO/Co_2O_3$ [19] and MnO_2 [20] have been reported. Though catalysts accelerated disappearance rate of target substances in all cases mentioned above, some of them were unstable in SCW and changed physically and chemically by hydrolysis like Cr_2O_3 to CrOOH. The stability is one of the key elements for heterogeneous catalysts as well as long-term activity because short-time stability regulates catalyst lifetime and it results in higher operational cost. In addition, additional treatment of the effluent may be needed if

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[*] Corresponding author. Tel.: +81 92 802 3431, fax: +81 92 802 3432.
E-mail address: f-takahashi@doc.kyushu-u.ac.jp (F. Takahashi).

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much leakage of heavy metals from the catalyst occurs. Although some of stable catalysts such as MnO_2–Mn_2O_3 have been reported [21], the authors focus on sodium titanate in this paper. Interestingly, sodium titanate can be synthesized hydrothermally under supercritical condition of targeted temperature less than 500 °C. The natural formation of sodium titanate means that it would be energetically advantageous form in SCW. Hence, sodium titanate is expected to be stable in SCW. In addition, it may be possible to re-activate and re-synthesize sodium titanate catalyst easily through the same operation of its synthesis when its deactivation and leakage from a reactor occur. Furthermore, the treatment of leaked titanium may not be needed to some extent because titanium is inactive metal in human body and the environment.

In this paper, catalytic activity of sodium titanate on the oxidation of acetic acid, its kinetics and re-activation by the same protocol as synthesis method will be provided.

2. Materials and methods

2.1. Catalyst preparation

Sodium titanate catalyst had been prepared before the oxidation of acetic acid was carried out. Particles of sponge titanium (Toho titanium Inc., Japan, purity >98%, ϕ0.84–1.68 mm) were placed 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). While 3.50×10^{-3} mol-Na/L (in ambient) of sodium carbonate solution was feed into the reactor at 25 MPa, 450 °C, about 7.2 s of residence time and for 5 h, sodium titanate crystals were hydrothermally synthesized on the surface of titanium particles. 15 percent of supplied sodium was converted into sodium titanate, which is corresponding to 1.98×10^{-4} mol-Na/g-Ti. After the reactor was depressurized and cooled, 350 ml of pure water was fed into the reactor for surface cleaning under ambient condition. Some of titanium particles, which colored whitely due to sodium titanate, were sampled for elemental composition analysis and surface area measurement.

2.2. Experimental apparatus

Experimental apparatus consisted of high-pressure pumps (NP-CX; Nihon Seimitsu Kagaku Inc., Japan), pre-heating 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 SUS 316 tubing (2.10 mm inner diameter, 5 m length, internal volume of 18.7 ml) was used in uncatalyzed oxidations and a reactor with 7.05 mm inner diameter was used in catalyzed oxidations (Fig. 1). Acetic acid and sodium carbonate 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 source of oxygen through its complete decomposition to oxygen and water at pre-heating part. Pure water was degassed by nitrogen gas before use. Solution of a reagent and hydrogen peroxide were fed separately into the reactor at 25 MPa and heated to targeted temperature (400–475 °C) in pre-heating line. Fed solutions were mixed before the reactor and passed through it at the residence time of 1.7–104 s. After the effluent were cooled and depressurized, liquid and gas samples were collected at the sampling port using glass container and gas bag, respectively.

2.3. Analysis methods

2.3.1. Characterization of synthesized catalyst

Elemental composition of synthesized catalyst was analyzed by scanning electron microscope-electron probe microanalyzer (SEM-EPMA, JXA-8200; JEOL Inc., Japan). Surface area of the catalyst was measured by surface analyzer (TriStar-3000; Micrometrics Inc., USA) using krypton gas as adsorbate.

2.3.2. Measurement of liquid and gas components

Concentrations of unreacted acetic acid and intermediates in the effluent liquid samples were analyzed by ion chromatography (IC-500; Shimadzu Inc., Japan) and high performance liquid chromatography (HPLC, HP series 1100; Hewlett-Packard Inc., USA). Total organic carbon (TOC) concentration was measured by TOC analyzer (TOC-500; Shimadzu Inc., Japan). To evaluate the stability of synthesized catalyst during SCWO, sodium concentration and titanium concentration in the effluent was also measured by ion chromatography (IC-500; Shimadzu Inc., Japan) and inductively coupled plasma mass spectrometry (HP4500; Yokogawa Analytical Systems Inc., Japan), respectively. When initial feed concentration of acetic acid was 9.54×10^{-5} mol/L or more in the reactor, concentrations of carbon dioxide, carbon monoxide, and methane in gas samples were measured by gas chromatography (IC-500;

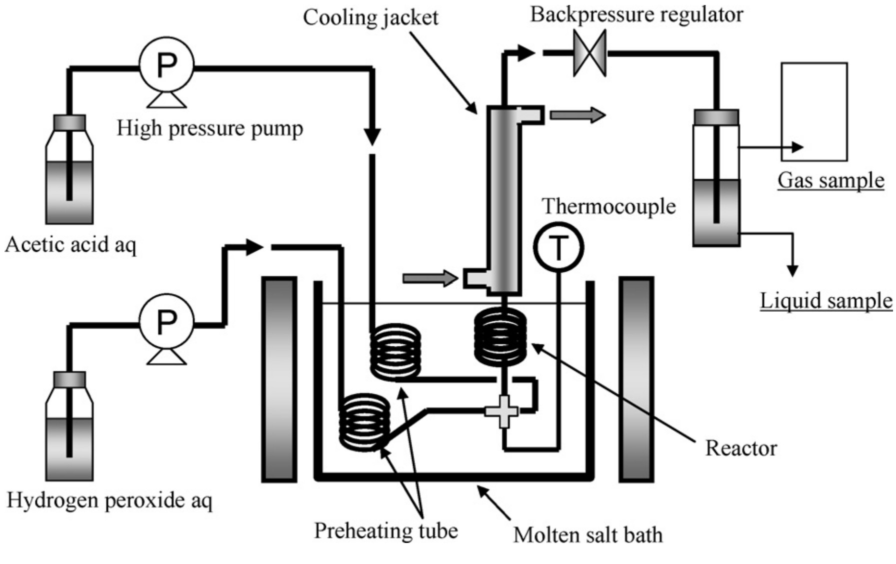

Fig. 1. Experimental apparatus of catalyzed/uncatalyzed SCWO.