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Oxidation of aliphatic alcohols and benzyl alcohol by H_2O_2 under the hydrothermal conditions in the presence of solid-state catalysts using batch and flow reactors

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HIGHLIGHTS

- Oxidation of alcohols under the hydrothermal conditions with H_2O_2 and solid-state catalyst.
- Environment harmless oxidation of benzyl alcohol and formaldehyde.
- Selective oxidation of benzyl alcohol to benzaldehyde by tungstate and metal deposited catalysts.
- Enhancement for the oxidation of formaldehyde by zeolite.
- Real-time monitoring oxidation of benzyl alcohol by hydrothermal flow reactor.

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ABSTRACT

Oxidation combining three key technologies—reaction with H_2O_2, hydrothermal processing, and solid-state catalysis—is attractive for the development of environmentally friendly processes. However, the combination of these technologies has not been extensively investigated. We evaluated the potential for environmentally friendly oxidation of alcohols using H_2O_2 under hydrothermal conditions in the presence of several types of solid-state catalysts. The reactions were investigated using both a conventional batch reactor and a hydrothermal micro-flow reactor (HMFR), which was originally developed by our group for monitoring reactions with time scales within 0.002–200 s at temperatures of up to 400 °C. The oxidation of methanol, ethanol, propanol, and butanol to carboxylic acids using H_2O_2 did not readily proceed at 120 °C, unlike the oxidation of formaldehyde to formic acid. The catalytic effect of tungstate in the oxidation was observed, and the observation of near infrared (NIR) spectra at 2050–2040 nm indicated that zeolite possesses a catalytic property in the oxidation of formaldehyde to formic acid. Conversely, H_2O_2 was effective for oxidation of benzyl alcohol to benzaldehyde and benzoic acid at 120 °C and higher temperatures. The selective catalytic properties of tungstate and platinum group metal-deposited catalysts were observed in the oxidation of benzyl alcohol to benzaldehyde. The oxidation reaction was successfully detected using an HMFR with a reaction time of 0.64 s at 300 °C. This study demonstrates the potential and usefulness of the environmentally friendly combination of H_2O_2, hydrothermal conditions, and solid-state catalysis for the oxidation of aromatic and aliphatic alcohols.

1. Introduction

In response to the demands of global environmental protection, the development of environmentally friendly technologies that do not depend on toxic chemicals is essential. Organic synthesis in aqueous solution is a technology with potential to replace conventional synthetic organic processes in organic solvents. Thus, the

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replacement of several types of conventional organic synthesis by such aqueous processes has previously been attempted. Recently, the possibilities for the use of extremely high-temperature aqueous solutions as environmentally harmless solvents have been investigated, focusing on their potential to provide efficient, rapid, and alternative pathways to those of aqueous reactions in synthetic processes at low temperatures [1–5]. However, hydrothermal reactions have been extensively applied in syntheses of inorganic materials [6,7].

Alcohol oxidation reactions are frequently important as fundamental steps in laboratory and industrial-scale chemical processes [8–11]. However, the oxidizing agents often used in industrial processes, such as manganates and chromates, are regarded as environmentally harmful. Thus, the advantages of environmentally friendly oxidizing agents, such as H_2O_2 and O_2, have been extensively studied. H_2O_2 is attractive for producing active oxidation species in aqueous solution, with H_2O as a by-product. For example, oxidation of lignin using H_2O_2 under hydrothermal conditions to produce organic acids has been attempted [12]. Furthermore, the screening of high performance solid-state catalysts, which are recoverable and do not readily diffuse into the environment, is a central issue for development of efficient chemical processes [11,13].

Thus, the investigation of applications combining the three environmentally benign techniques of H_2O_2 oxidation, hydrothermal conditions, and solid catalysts, has great potential for the development of new environmentally friendly reaction processes that dispense with the need for toxic reagents. However, such investigations are yet to be extensively performed. It is necessary to investigate hydrothermal reactions with extraordinary efficiency, high throughput analysis, and convenient procedures in the presence of solid phase catalysts. However, it is difficult to obtain a result combining these three factors. Such problems have inhibited the development of practical environmentally friendly applications using hydrothermal reactions in the presence of solid-state catalysts.

We have developed a series of hydrothermal micro-flow reactors that simulate hydrothermal environments on the primitive Earth, for investigation of the evolution of chemical processes under such conditions [14–18]. The hydrothermal flow systems enable reaction processes in aqueous solutions to be monitored within 0.002–200 s at temperatures of up to 400 °C, with in situ observation of UV–VIS absorption spectra. In addition, we have recently established the principle and experimental setup for the flow reactor systems in the presence of solid particles, namely the mineral-mediated hydrothermal micro-flow reactor, which enables the monitoring of hydrothermal reactions within 3–210 s at temperatures of up to 275 °C [18]. Applications of the technology are expected to be used in fundamental and practical areas related to global environmental protection, such as enhancement of the oxidation reactions of alcohols mentioned above using solid-state catalysts. Thus, we commenced examination of potential roles of the hydrothermal flow reactor technologies for organic reactions in aqueous solutions.

Although extensive investigations have been made of the oxidation of alcohols at low temperatures in aqueous solutions in the presence of solid-state catalysts [19–26], such reactions under hydrothermal conditions have, to our knowledge, never been the focus of study. Thus, as a first step towards development of a research tool for practical application of hydrothermal reactions, using the principle of the mineral-mediated hydrothermal micro-flow reactor, we present the first report of oxidation reactions of benzyl alcohol and aliphatic alcohols to aldehydes and carboxylic acids in the presence of H_2O_2 and several potential catalysts under hydrothermal conditions. The potential catalysts, such as soluble tungstate, solid-state platinum metal-deposited particles, and metal ion-deposited particles, which would act as catalysts for the oxidation reaction under the hydrothermal conditions, were examined using ultraviolet–visible (UV–VIS) and near infrared (NIR) absorption spectra [27]. In addition, we briefly demonstrate the usefulness of in situ UV–VIS observations using the micro-flow reactor system.

2. Experimental

2.1. Reagents

Benzoic acid, benzaldehyde, methanol, ethanol, 1-propanol, 1-butanol, $Na_2WO_4 \cdot H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, NH_4VO_3, $NaNbO_3$, zeolite (HS-320), silica gel (Wakogel® C-200, 0.075–0.15 mm), MoO_3, and activated alumina (0.045–0.15 mm) were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Iridium, 5% on calcium carbonate powder, rhodium, 1% on alumina powder, reduced, palladium, 1% on alumina powder, reduced, platinum, 1% on γ-alumina powder, reduced, ruthenium, typically 5% on alumina powder, reduced, and pyrite were purchased from Alfa Aesar (Johnson Matthey Company, Japan). All other reagents used were of analytical grade. These samples were dissolved or suspended for the preparation of reaction mixtures in double distilled water.

2.2. Apparatus

Reaction behaviors were investigated using a high temperature and pressure resistant reactor (HU-25, Sanai Kagaku, Japan), and a hydrothermal micro-flow reactor (HMFR) that was originally developed by our laboratory. The HMFR consists of a water reservoir, high-pressure pump, sample injector, high temperature reactor, cooling bath, pressure regulator, and temperature controller (Fig. 1) [14–18]. The HMFR enables the monitoring of hydrothermal reactions within the millisecond to second time scale, at temperatures of up to 400 °C. The reactions were carried out using Sulfinert tubing with an inner diameter of 0.25 mm (GL Sciences Inc. Japan; effective volume 1.38×10^{-1} cm^3 for heating) and fused-silica capillary tubing with an inner diameter of 0.1 mm (GL Sciences Inc. Japan; effective volume 2.67×10^{-3} cm^3 for heating). By connection of a UV–VIS detector (200–600 nm) with the fused-silica capillary tubing via optical fibers, in situ monitoring at high temperatures can be performed. The residence time of exposure at high temperatures using the HMFR is defined as reaction time. The detail setup of the in situ monitoring system is outlined in a previous publication [17].

Products were analyzed using a UV–VIS-NIR spectrophotometer (V-670, JASCO, Japan) and a high performance liquid chromatograph (HPLC). UV absorption spectra at 200–350 nm were measured for the reaction behavior of benzoic acid, and the NIR absorption spectra for the reaction behavior of aliphatic alcohols at wavelengths higher than 2000 nm were primarily measured. HPLC analysis of the benzoic acid reaction was carried out using a LC10A system, Shimadzu, Japan on a reversed-phase column (CAPCELL Pak C18 UG120, 2.0 mm (inner diameter) × 10 cm, Shiseido, Japan) and a guard column (CAPCELL Pak C18 UG120, 2.0 mm (inner diameter) × 3.5 cm, Shiseido, Japan) with an eluent containing 0.075 M NaH_2PO_4 in an aqueous medium of 25% methanol at a flow rate of 0.2 mL/min. Detection of the products of benzoic acid reaction was performed at 212 nm or 250 nm. Dissolved oxygen was monitored using a dissolved oxygen meter (Orion 5 Star, Thermo Fisher Scientific, Inc.).

2.3. Preparation of catalysts

Some potential catalysts were prepared by the deposition of $Na_2WO_4 \cdot 2H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, or NH_4VO_3 solutions on silica