



Preparation of porous paper composites with ruthenium hydroxide and catalytic alcohol oxidation in a multiphase gas–liquid–solid reaction



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ABSTRACT

In situ synthesis of ruthenium hydroxide catalysts on a microporous fiber-network structure of ceramic paper composites was achieved. The efficient catalytic oxidation of alcohol was investigated in a heterogeneous, multiphase gas–liquid–solid reaction. A simple papermaking technique and subsequent immersion in a ruthenium chloride solution allowed us to fabricate novel-concept microstructured catalysts. The paper-structured catalysts possess micropores *ca.* 30 μm in diameter with high porosity of *ca.* 90%. They exhibited much higher catalytic efficiency in the O_2 -mediated oxidation in toluene of benzyl alcohol to benzaldehyde in a fixed bed external loop reactor, as compared with conventional pellet- and bead-type solid catalysts. This excellent catalytic effect is possibly attributed to the porous paper composite microstructure like microreactors.

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1. Introduction

Catalysts play an indispensable role in the efficient mass manufacture of energy and products, resulting in catalyst research and development being promoted with great interest [1]. In particular, the catalytic oxidation of alcohols to provide the corresponding carbonyl compounds is one of the most important reactions in chemical industries, because of the extremely broad application of these oxidized products as major intermediates for medicines, fertilizers and various chemicals [2,3]. Traditional synthesis has been performed using toxic inorganic oxidants such as chromium (IV) and manganese (VII); however, from both economic and environmental viewpoints, there have been demands to achieve greener processes that operate at lower temperatures using cleaner oxidants such as O_2 and H_2O_2 [3,4]. A variety of homogeneous and heterogeneous catalysts have been developed for the O_2 -mediated alcohol oxidation processes [5,6]. Homogeneous catalysts have several advantages of efficiency, selectivity and yields; however, their use in industrial applications is strictly limited because of difficulties in the separation of used catalysts from final products. Therefore, in practical applications, heterogeneous catalysts

in solid form are sought after to effectively perform in complex multiphase mixtures of gas (air/ O_2), liquid (substrates/media) and solid (fixed catalyst).

The most popular use of heterogeneous catalysts in industry for liquid and multiphase applications is in slurry-type reactors. Small catalyst particles are stirred in a vessel to a quasi-homogeneous state, minimizing temperature and concentration gradients [7]. However, the slurry reactors have several disadvantages: (1) difficult separation of products from the finer catalysts because of catalyst attrition, (2) inevitable abrasion of the process equipment by moving hard particles, and (3) low productivity and complicated operation in continuous processes. Therefore, fixed bed reactors are required as an alternative to slurry reactors, and have been applied widely in current industries [8]. Particle packed bed reactors are typical items of equipment, and there are no issues for the separation of products from catalysts, because all catalysts are fixed strongly on the beds. Although the simple structure and low operating cost are beneficial [7], the particle packed bed reactors display critical disadvantages because of (1) large particle sizes, (2) high pressure drops and low mass transfer efficiencies in the gas–liquid–solid phases, (3) complicated temperature control and the uncontrollable generation of hot spots (exothermic reactions), and (4) additional demand on liquid and gas distributors [8]. Catalyst particle sizes larger than those in slurry reactors are undesirable for efficient heterogeneous catalysis, and eventually cause

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lower reactivity and selectivity because of intraparticle diffusion limitations and low specific surface area. Thus, balanced properties to reconcile the large interfacial reactivity and practical utility that slurry and packed bed reactors possess, respectively, are a major target to improve catalytic reaction engineering [9].

Recently, fixed bed reactors having micrometer-sized pore structures, termed microreactors, have attracted much attention in industrial circles because of improvements in mass and heat transfer inside the flow path at a micrometer scale [10]. Various types of microreactors such as honeycomb [11], foam [12] and string assembly [13] reactors have been investigated, and fibrous catalysts especially are expected to satisfy the requirements of high catalytic efficiency and low pressure drop. Fine catalyst particles fixed on the boundary surfaces forming microflows would enable high geometrical surface area, short diffusion distance and smooth flow in the gas–liquid–solid phases. Further advances in the structural and functional design of microreactors using carbon, glass and ceramic fibers instead of expensive metal fibers would provide a new insight and approach to realize the practical applications of fibrous microreactors [14]. In our previous studies, paper-like catalysts composed of inexpensive ceramic fibers were developed by a high-speed and low-cost papermaking technique. As-prepared paper composites, termed paper-structured catalysts, are easy to fabricate and handle and possess porous microstructures derived from layered fiber networks such as paper [15–18]. Cu/ZnO catalyst powders were loaded into a paper matrix and demonstrated efficient catalytic hydrogen production from methanol in the gas phase [15]. Direct *in situ* synthesis of Au nanoparticles on a microstructured paper matrix composed of ceramic fibers and ZnO whiskers was achieved, and showed excellent performances for low temperature gas phase CO oxidation [16] and for liquid phase 4-nitrophenol reduction [17]. Pt nanocatalysts were synthesized on surface-activated carbon fibers, and exhibited a high removal efficiency of NO_x and CH₄ from exhaust gases [18]. These results suggested that the unique porous microstructures of the paper-structured catalysts must play significant roles in two phase reactions such as gas–solid [15,16,18] and liquid–solid reactions [17].

In this study, a new type of paper-structured catalyst was prepared using ruthenium hydroxide (Ru(OH)_x) and alumina/silica (Al₂O₃/SiO₂) fibers by our established papermaking technique, and first applied to multiphase catalysis for efficient alcohol oxidation. Much attention has focused on Ru(OH)_x as a promising alcohol oxidation catalyst, and the aerobic oxidation of alcohols has been reported using Ru(OH)_x on hydroxyapatite [19], Ru(OH)_x on TiO₂ [20,21], Al₂O₃ [22], silica [23], and Fe₃O₄ [24]. However, few studies have been devoted to develop the structured catalysts toward practical applications [25–27]. Herein, inexpensive commercial Al₂O₃-rich ceramic fibers were fabricated into a paper matrix, followed by the impregnation of Ru(OH)_x via the on-paper synthesis approaches [16–18]. As-prepared Ru(OH)_x/Al₂O₃ paper composites with a porous microstructure were characterized by scanning electron microscopy (SEM), atomic absorption spectrophotometry (AAS) and other instrumental analysis. The catalytic conversion of benzyl alcohol to benzaldehyde in multiphase aerobic oxidation (O₂ fed into toluene) was investigated using a fixed bed external recycling loop reactor, as compared with pellet and bead catalysts without any microstructures.

2. Experimental

2.1. Materials

Ceramic fibers (DENKA ALCEN B80L, Al₂O₃: 80% and SiO₂: 20% by weight, Denki Kagaku Kogyo Kabushiki Kaisha, Tokyo, Japan) were

cut into an average length of ca. 0.5 mm using a four-flute end mill. An alumina sol (520, Nissan Chemical Industries Ltd, Tokyo, Japan) was used as an inorganic sol binder to improve the physical strength of the catalyst papers, and also as a catalyst carrier. Two types of flocculants were used as retention aids; polydiallyldimethylammonium chloride (PDADMAC; molecular weight: ca. 3 × 10⁵; charge density: 5.5 meq g⁻¹; Sigma–Aldrich Co. LLC, St. Louis, MO, USA) and anionic polyacrylamide (A-PAM, A125S; molecular weight; ca. 1 × 10⁷; charge density: 3.2 meq g⁻¹; MT Aquapolymer, Inc., Tokyo, Japan). Pulp fibers, as a tentative supporting matrix in the paper-making process, were obtained by beating commercial bleached hardwood kraft pulp to 300 ml of Canadian Standard Freeness with a Technical Association of Pulp and Paper Industry (TAPPI) standard beater, according to our established preparation method [15–18]. Gamma-alumina powder and beads as catalyst supports were purchased from Sumitomo Chemical Co. Ltd, Tokyo, Japan (powder: A-11, beads: KHS-24). The Ru(OH)_x catalysts in powder and bead form were prepared and tested according to literature procedures [22]. Catalyst pellets 3 mm in diameter × 5 mm in height were molded using a tablet machine (AUTOTAB-500, ICHIHASHI-SEIKI Co. Ltd., Kyoto, Japan). Other chemicals were reagent grade and were used without further purification.

2.2. Preparation of paper-structured catalysts

A water suspension of ceramic fibers was mixed with PDADMAC (0.5 wt% of total solid), alumina sol and A-PAM (0.5 wt% of total solid), in that order, with each step being performed at an interval of 3 min. The mixture was added to the pulp fiber suspension, and paper composite sheets were prepared according to our previous reports [15–18]. The wet state sheets were pressed at 350 kPa for 3 min, and then oven dried at 105 °C for 1 h. The resulting paper composites (2 × 10⁴ mm²) consisted of ceramic fibers (5.0 g), alumina sol (0.54 g) and pulp fibers (0.25 g). The paper composites obtained were calcined at 600 °C for 5 h to remove organic pulp fibers and to improve the physical strength by alumina binder sintering.

On-paper synthesis of Ru(OH)_x on an as-prepared paper matrix was carried out in the following sequence. First, paper composites were cut into disc-shaped pieces (diameter: 23 mm) and immersed in an aqueous solution of ruthenium chloride (RuCl₃; 8.3 mM, 50 mL) for 5 h. The discs were then removed from the solution using tweezers, and oven dried at 105 °C for 1 h. In the second step, the discs were immersed in an aqueous solution of RuCl₃ (8.3 mM, 50 mL) for 24 h, and the solution pH was adjusted to 13 by the addition of an aqueous solution of NaOH (1.0 M). The discs were removed from the solution, washed with deionized water, and dried at 105 °C for 1 h.

2.3. Characterization

Specific surface areas were obtained from nitrogen absorption–desorption isotherms (BELSORP-mini, BEL Japan Inc.). The specific surface areas were calculated by the Brunauer–Emmet–Teller (BET) method. Surface observation of the paper-structured catalysts was performed by SEM (S-4300SE/N, HITACHI High-Technologies Corporation), and elemental mapping was also obtained by energy dispersive X-ray spectrometry (EDS, EMAX-500, HORIBA Ltd). Mercury intrusion analysis was carried out using an AUTOPORE IV 9500 (Micrometrics Instrument Corporation). Pore size distribution was obtained from a pressure-cumulative mercury intrusion volume curve normalized by each catalyst weight. The Ru content was determined by AAS (AA-6600F, Shimadzu, Co. Ltd.). The concentration of Ru ions eluted from the samples with hydrochloric acid was measured.

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