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Selective oxidation of benzyl alcohol using RuHAp-containing sheet composites

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Abstract Ru-containing hydroxyapatite (RuHAp) powder was successfully impregnated into sheet composites using a papermaking technique, and its catalytic efficiency was investigated. The RuHAp powder was homogeneously scattered over the fiber-mix networks that had been tailored within the catalyst sheet. RuHAp-containing sheets demonstrated superior performance to RuHAp beads for the selective oxidation of benzyl alcohol to benzaldehyde in a batch reaction process and the efficiency was equivalent to that of RuHAp powder. Catalytic performance was also evaluated in a continuous fixed-bed column reactor and RuHAp sheets showed higher oxidation efficiency than both RuHAp powder and beads. The porous structure of composites seemed to improve the effective transport of benzyl alcohol to RuHAp surfaces which were immobilized within the sheets, resulting in enhanced catalytic performance.

Introduction

A sustainable society requires the development of green chemistry which aims to reduce or eliminate by-products and wastes formed during chemical reactions. The preparation or improvement of catalysts that have enhanced activity and high selectivity is strongly desired. Homogeneous catalysts such as metal complexes and enzymes show high selectivity under relatively mild conditions compared with heterogeneous catalysts. This is due to their strictly controlled structures and they are thus able to suppress undesirable by-product formation. Recovery and recycling of homogeneous catalysts from reaction media is, however, difficult and expensive, but immobilization onto suitable organic or inorganic supports has been carried out energetically [1–5].

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is a type of calcium phosphate and has attracted attention as a metal catalyst support due to its ion-exchange ability [2–4, 6, 7]. HAp has a hexagonal crystal structure and Ca^{2+} in the lattice can be exchanged for other cations like Ru^{3+} and Pd^{2+}. Yamaguchi et al. reported the first preparation of Ru-immobilized HAp (RuHAp) powder and its application to the selective oxidation of alcohols in the liquid phase [2]. Selective oxidation of alcohols is an important reaction and synthesized aldehydes serve as raw materials for various chemicals. Primary alcohols may be converted to their corresponding aldehydes by RuHAp with high selectivity using molecular oxygen as a safe and inexpensive oxidant. It has been reported that the RuHAp catalyzes not only alcohol oxidation but is also used for the dehydrogenation of amines and the hydrogenation of nitriles; thus, RuHAp powder is a promising heterogeneous catalyst having unique catalytic properties [4]. For practical application, however, effective fabrication methods of the inconvenient powdery catalysts are being investigated [8].

We have previously reported the preparation of sheet-like composites containing powders such as a Cu/ZnO catalyst for hydrogen production, TiO_2 photocatalysts, and zeolite adsorbents using the papermaking technique [9–13]. The prepared sheets were easily handled and showed enhanced catalytic performance. In this study, RuHAp-containing sheet composites were prepared in a similar manner and their catalytic performance in a selective oxidation reaction was compared with the reactions of the powder and bead

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catalysts. Furthermore, the catalytic efficiency as applied to a continuous fixed-bed column reactor was also evaluated.

Experimental

Materials

HAp beads (diameter: 3–5 mm; porosity: 10%; ECCERA Co. Ltd.) were used; they were pulverized, in part, to a 100-mesh pass powder using a bowl mill. $RuCl_3 \cdot nH_2O$, benzyl alcohol, benzaldehyde, and acetonitrile were reagent grade and purchased from Wako Pure Chemical Industries, Ltd. Glass fibers (CMLF208, ca. 0.8 μm diameter, Nippon Sheet Glass) were used as the sheet matrix and was cut into ca. 0.5 mm length on average before use. Pulp fibers supporting the wet-web during the dewatering stage of the papermaking process was bleached hardwood kraft pulp that had been beaten to 500 mL of Canadian Standard Freeness according to the Technical Association of the Pulp and Paper Industry (TAPPI) Test Methods T200 and 227 with a standard beater for paper sheet making. Poly (diallyldimethylammonium chloride) (PDADMAC, molecular weight (M_w): ca. 3×10^5; charge density (CD): 5.5 meq g^{-1}; Aldrich, Ltd.) and anionic polyacrylamide (A-PAM, HH-351; M_w: ca. 4×10^6; CD: 0.83 meq g^{-1}; Kurita, Ltd.) were used as flocculants for handsheet making with a dual polymer retention system.

Preparation of RuHAp-containing sheet composites

RuHAp powder was prepared according to previous reports [2–4]. HAp (2.5 g) in 200 mL deionized water was mixed with 25 mL of 19.8 mM aqueous $RuCl_3$ solution (Ru ca. 50 mg) for 10 min. The resultant slurry was filtered, washed with deionized water, and dried in an oven at 105 °C for 1 h giving RuHAp as a black powder (Ru 2 wt%). RuHAp bead was also prepared using HAp bead.

The RuHAp sheet was prepared using two types of flocculants as follows: a suspension of glass fibers (5.0 g) and RuHAp (2.5 g) was mixed with PDADMAC (0.00–0.50% total solid) followed by the sequential addition of A-PAM (0.00–0.50% total solid) at 3-min intervals. Subsequently, the mixture was poured into a pulp (0.5 g) suspension and the handsheets with a grammage of 128 gm^{-2} were prepared according to the TAPPI Test Method T205. After pressing at 350 kPa for 5 min, the wet sheets were dried in an oven at 105 °C for 30 min.

Selective oxidation of benzyl alcohol to benzaldehyde

The batch experiment was performed as follows: the benzyl alcohol solution (1 mM, 3 mL) prepared with acetonitrile was poured into a glass vessel. RuHAp sheet, RuHAp powder, or RuHAp beads with a Ru content of 0.5 mg was added to the reaction vessel. RuHAp retention was taken into account for the RuHAp sheet. The temperature of the reaction vessel was maintained at 30 ± 1 °C. A designated aliquot filtered with a membrane filter (Chromatodisk, pore size: 0.2 μm; GL Sciences, Ltd.) was used for high-performance liquid chromatography (HPLC). The HPLC analysis was carried out using a Gemini column (Phenomenex) and a UV detector at 254 nm with a linear gradient from 20% acetonitrile in deionized water (isocratic for 3 min) to 100% acetonitrile (11–21 min) at a constant flow rate of 1.0 mL min^{-1}. The coefficient of variance for HPLC was less than 5% based on three measurements. Reaction by-products were analyzed using GC-MS; the GC-MS analysis was performed with a JEOL Automass Sun 200 mass spectrometer at 70 eV fitted with an Agilent gas chromatograph and a 30 m fused silica column (HP-5, Agilent).

Selective oxidation was performed using a fixed-bed flow reactor; 30 pieces of circular RuHAp sheet, each with an area of ca. 7×10^2 mm^2 (30 mm diameter, Ru content of 0.5 mg) were placed on top of each other (7×10^3 mm^3) and put in a glass cylinder (30 mm inner diameter). RuHAp powder and beads each with a total volume of 7×10^3 mm^3 were also placed inside reaction cylinders. The total amount of Ru used in fixed-bed reactor was 15 mg. When powder was used inert HAp powder with equal particle sizes were mixed to adjust the occupied volume to 7×10^3 mm^3. Benzyl alcohol (0.1 mM) was introduced into the reactor using a pump at a constant flow rate of 1 mL min^{-1}. Reacted aliquots were subjected to HPLC for benzyl alcohol and benzaldehyde concentration measurements.

Other analyses

The substitution of Ru^{3+} for Ca^{2+} in HAp was confirmed by atomic absorption analysis and the Ru remaining in the supernatant of the RuHAp suspension was quantified. Scanning electron microscopy (SEM) of the RuHAp sheet surface was performed with a JEOL JSM-5510 LV apparatus after platinum coating. The electron accelerating voltage was set at 6 kV.

Results and discussions

Preparation of RuHAp-containing sheets by the papermaking technique

Figure 1 shows optical and SEM images of RuHAp-containing sheets. RuHAp powder was successfully fabricated into a sheet structure by a papermaking technique employing a dual polymer retention system [9–13]. The relationship

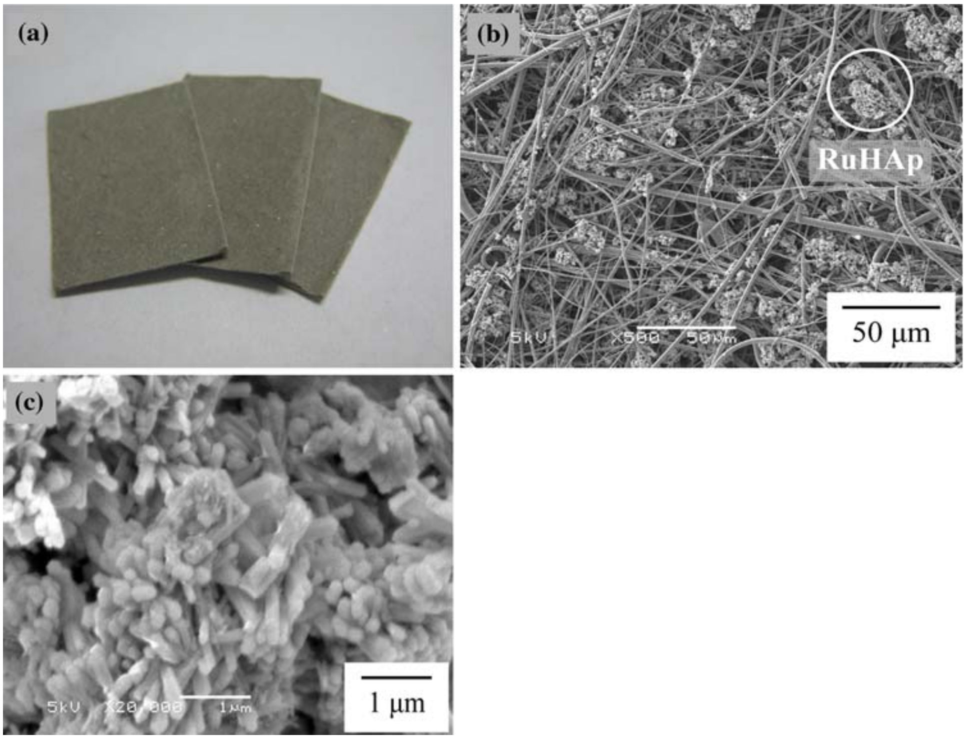

Fig. 1 Optical (**a**) and SEM images of RuHAp-containing composites (**b**) as well as the surface of RuHAp particles immobilized in sheet composites (**c**)

between flocculant dosage and RuHAp retention will be discussed further. RuHAp sheets, consist of glass and pulp fiber, are flexible and have the external appearance of cardboard. The small amount of pulp fibers that were mixed with the glass fibers played an important role in the wet-web formation during the dewatering process and in the practical application. The hydrogen bonds between pulp fibers improved the sheet strength enough to allow for handling in an organic solvent and thus RuHAp composites are more easily handled than the original RuHAp powder. Micrometer-sized particles having hexagonal crystal structures were scattered over the fiber-mix matrix as seen in Fig. 1c indicating that the HAp crystal structure was maintained after ion exchange and only surface Ca^{2+} was thus assumed to have been exchanged for Ru^{3+}.

Selective oxidation performance of RuHAp sheet composites

Figure 2 shows the time course of benzyl alcohol and benzaldehyde concentrations during selective oxidation by treatment with RuHAp sheets prepared with a flocculant dosage of 0.10%, RuHAp powder, and RuHAp beads. Each catalyst converted benzyl alcohol to benzaldehyde and the increase of benzaldehyde during the reactions corresponded to the decrease of benzyl alcohol. The oxidation mechanism for the use of RuHAp with molecular oxygen has previously been proposed in the literature; the reaction involved ligand exchange between benzyl alcohol and RuHAp and following β-hydride elimination to produce benzaldehyde [4]. No significant amounts of intermediates were detected by HPLC or GC-MS analysis and therefore the prepared catalysts selectively oxidized benzyl alcohol to benzaldehyde at 30 °C and under 1 atm air pressure.

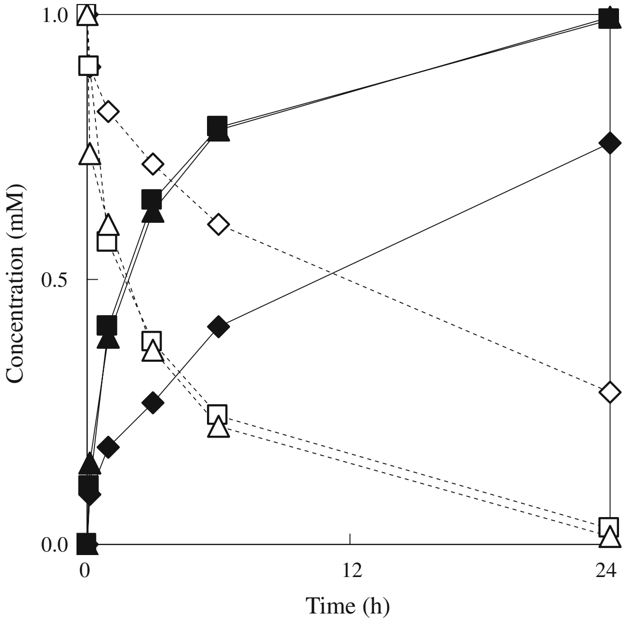

Fig. 2 Time course of benzyl alcohol (*open symbols*) and benzaldehyde (*closed symbols*) concentrations treated with a RuHAp sheet prepared with a flocculant dosage of 0.10% (*squares*), RuHAp powder (*triangles*), and RuHAp beads (*diamonds*)

The RuHAp sheets were better at the selective oxidation of benzyl alcohol than RuHAp beads and were equivalent to the RuHAp powder. The catalytic efficiency of molded or shaped catalysts such as beads, pellets, and rods with a typical sizes of 5–10 mm has been found to be lower compared to powdery catalysts due to intraparticle diffusion limitations [8]. TON of benzaldehyde treated by RuHAp sheet, powder, and beads were 0.60, 0.60, and 0.45, respectively. For RuHAp sheets, the small micrometer-sized RuHAp particles were homogeneously scattered within the sheets and intraparticle diffusion limitations were negligible. In addition, the macrostructure of catalysts have become a major point of interest and unique structure-independent effects on catalytic efficiency were recently reported, for example, the porosity and heat conductivity of supports greatly influence mass and heat transfer and thus catalyst efficiency [14–16]. The porous sheet structure seems to improve mass transfer of benzyl alcohol to the RuHAp surface inside the sheet resulting in improved performance. From these results it is clear that catalyst composites possessing both practical convenience and enhanced catalytic performance are promising for future catalyst-based materials.

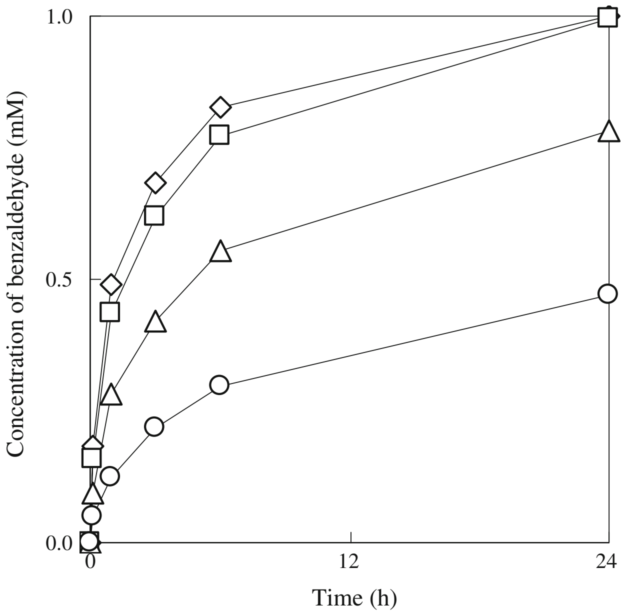

Fig. 3 Time course of benzaldehyde concentration formed in the catalytic reaction treated by RuHAp sheets with flocculant doses of 0.05% (*diamonds*), 0.10% (*squares*), 0.20% (*triangles*), and 0.50% (*circles*) on solid

The influence of flocculant dosage on RuHAp retention and catalytic efficiency

The RuHAp sheet composites were successfully prepared by a papermaking technique with a dual polymer retention system. The system is summarized as follows: PDADMAC macromolecules with a large cationic charge are adsorbed onto suspended RuHAp particles and glass fibers having a small negative charge in an aqueous system. A-PAM chains with high M_w then allow bridging between the positively overcharged inorganics. Powder retention is known to improve with an increase of added flocculant during the sheet forming process and therefore the relationship between flocculant dosage and RuHAp retention on catalytic performance was investigated. In this study, the retention of RuHAp powder increased with an increase of flocculant dosage and the RuHAp sheet samples with flocculant dosages of 0.00, 0.05, 0.10, 0.20, and 0.50% on the solid were 63.2, 85.5, 90.0, 94.5, and 94.8%, respectively. The dual polymer retention system in which cationic and anionic flocculants are combined was clearly significant for RuHAp retention. Figure 3 displays the time course of benzaldehyde concentration as formed by the selective oxidation with RuHAp sheets at different flocculant dosages. Ru content was adjusted to 0.5 mg by changing the amount of the sheet used in the reaction. The catalytic efficiency was drastically influenced by flocculant dosage and higher flocculant doses deteriorated catalytic performance. The concentration of benzaldehyde after 24 h of treatment using RuHAp sheet with 0.50% flocculant dosage was ca. 0.5 mM which is about half that obtained using a sheet with 0.10% flocculant dosage, although the same amount of Ru was used. When PDADMAC and A-PAM were added to RuHAp powder the catalytic performance decreased compared with untreated RuHAp powder (data not shown). Contact between benzyl alcohol and RuHAp was assumed to be inhibited by flocculant adsorption onto the surface of RuHAp resulting in decreased catalytic performance. In the case RuHAp sheet with 0.05 or 0.10% flocculant dosage, catalytic efficiency was equivalent or somewhat lower in performance compared to RuHAp powder; thus, negative effect of flocculant on performance seemed to be small enough to be negligible. From the viewpoint of both RuHAp retention and catalytic efficiency, the optimum flocculant dosage was determined to be 0.10% on solid.

Catalytic conversion using a fixed-bed reactor

RuHAp sheet composites are filter paper-like materials (Fig. 1) with liquids able to pass through the porous sheet. The selective oxidation of benzyl alcohol was, therefore, examined in a continuous system using a fixed-bed reactor. RuHAp sheets, powder, and beads were placed in a fixed-bed reactor and their catalytic efficiencies were compared. Figure 4 shows the relationship between elution volumes of reaction media from the reactor and benzyl alcohol conversions. The yields of benzaldehyde were similar to

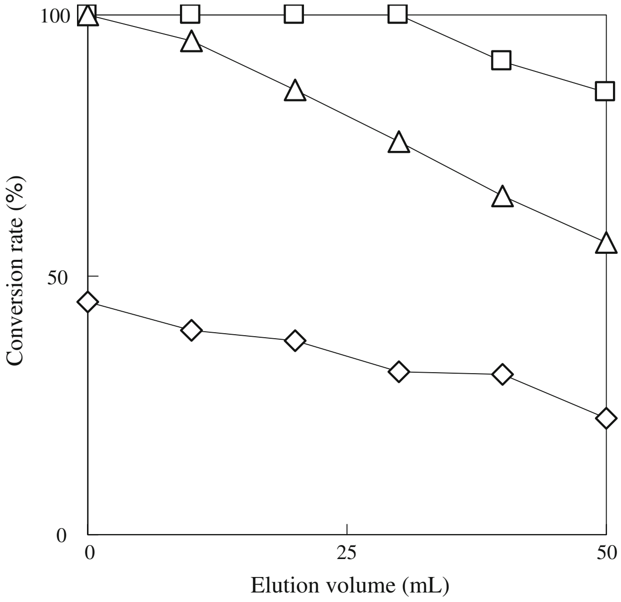

Fig. 4 The relationship between elution volume of reaction media from the fixed-bed reactor and benzyl alcohol conversions when treated with RuHAp sheets (*squares*), powder (*triangles*), and beads (*diamonds*)

the yields in the batch process. Sheet composites exhibited the highest conversion efficiency among the three types of catalysts and this did not correspond to the results of the batch experiments. For the powder or bead catalysts, heterogeneous catalyst filling in the fixed-bed reactor seemed to cause a large pressure drop and fluid by-passing which deteriorated their catalytic efficiency. On the other hand, uniform micrometer-sized pores inside RuHAp sheet composites allowed for good permeation of the reaction medium resulting in higher conversion efficiency. The porosity of sheet composites and the RuHAp content were controllable to some extent by the wet papermaking process and therefore RuHAp sheets having suitable structures for continuous reactors can be prepared easily [12].

Conclusion

RuHAp-containing sheet composites were successfully prepared using a wet papermaking technique and were applied to the selective oxidation of an alcohol. The porous RuHAp sheet was easily handled and may be used in an organic solvent. The alcohol conversion efficiency of RuHAp sheets was superior to that of shaped RuHAp beads and equal to that of a powdery catalyst in a batch reaction system. RuHAp sheets showed superior alcohol conversion compared with the powdery catalyst in a continuous fixed-bed reactor system. The porous sheet structure seemed to improve mass transfer within the sheet resulting in enhanced catalytic efficiency. The sheet structure is adjustable to some extent by the wet papermaking process and thus RuHAp-containing sheets that are both practically convenient and show sufficient catalytic performance are promising materials for continuous chemical reactions.

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