Chemical Engineering Journal 157 (2010) 311–315

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Preparation of ruthenium-containing sheet composites using a papermaking technique for selective oxidation of alcohol

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ARTICLE INFO

*Article history:*
Received 28 April 2009
Received in revised form 7 October 2009
Accepted 30 October 2009

*Keywords:*
Catalyst sheet
Papermaking technique
Ruthenium
Ion-exchange
Selective oxidation

ABSTRACT

Ruthenium (Ru) catalyst was introduced onto a glass fiber surface by ion-exchange, the treated fibers were made into Ru-containing sheet composites (referred to in this paper as Ru sheets) using a papermaking technique. Ru was easily introduced by mixing $RuCl_3$ aqueous solution into a glass fiber suspension and became strongly attached and immobilized on the fiber surface. Ru sheet is easy to handle and is strong enough to use for chemical reactions in organic solvents. X-ray photoelectron spectroscopy and atomic adsorption analyses revealed that the Ru attachment was not simple adsorption but due to an ion-exchange mechanism. Pieces of Ru sheet were used to catalyze selective oxidation of benzyl alcohol to produce acetaldehyde and demonstrated a higher performance than commercial Ru-containing catalyst powders. The porous sheet structure seemed to improve the effective transport of benzyl alcohol to inside of the sheet, resulting in enhanced catalytic performance. Thus Ru sheet demonstrates both practical convenience and a high level of catalytic activity when compared with currently available alternative materials.

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## 1. Introduction

To assist the development of a sustainable society, a changeover to "green chemistry", reducing or eliminating by-products and waste formed during chemical reactions is a necessity. The improvement of catalyst activity and selectivity is an obvious step along this path. Metal complex catalysts such as ruthenium (Ru) and palladium (Pd) show high selectivity due to specific nature of their atomic structures and hence, when used as catalysts suppress undesirable by-product formation. In addition, they are able to catalyze reactions under relatively mild conditions compared with heterogeneous catalyst equivalents. However, the recycling of metal complex catalysts from reaction media is difficult and expensive.

Recently, the immobilization of metal complex onto suitable inorganic substrates through ion-exchange, for example Ru- or Pd-containing hydroxyapatite and hydrotalcite has been reported [1–6]. Kaneda et al. [1,3] reported the first preparation of Ru-hydroxyapatite (RuHAp) powder and its application to the selective oxidation of alcohols, in the dehydrogenation of amines and the hydrogenation of nitriles in the liquid phase. These metal complex containing catalysts are promising materials as they have catalytic activity as a homogenous catalyst and are as easily recovered as a heterogeneous catalyst. For practical application however, powder catalyst is inconvenient due to its small particle size, so effective fabrication methods using powdery catalysts are being investigated [7].

We have previously reported the preparation of sheet-like composites containing various catalyst powders using papermaking techniques [8–13]. The prepared sheets were easily handled and showed enhanced catalytic performance compared with molded catalysts, indicating that catalyst sheets are promising catalytic materials. In this study, Ru was directly introduced onto silicate glass fiber used in papermaking by ion-exchange, then an Ru-containing sheet composite (Ru sheet) was prepared in a similar manner. The Ru sheet was then tested by application to a selective oxidation reaction and its catalytic performance was compared with the reactions of commercial Ru-containing powder catalyst.

## 2. Experimental

### 2.1. Materials

Glass fibers (CMLF208, ca. 0.8 μm diameter, Nippon Sheet Glass) were used as the sheet matrix after being cut into nominal 0.5 mm lengths. The pulp fibers used to support the wet-web during the dewatering stage of the papermaking process were bleached hardwood kraft pulp that had been beaten to 500 ml of Canadian Standard Freeness using the Technical Association of the Pulp and

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doi:10.1016/j.cej.2009.10.063

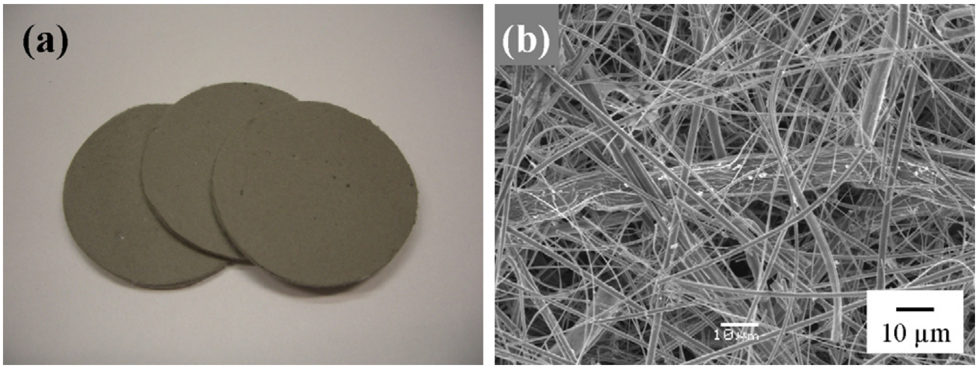

**Fig. 1.** Optical (a) and SEM (b) images of Ru sheet.

Paper Industry (TAPPI) Test Method with a standard beater for paper sheet manufacture [14,15]. $RuCl_3 \cdot nH_2O$, benzyl alcohol, benzaldehyde, acetonitrile and Ru-hydroxyapatite (RuHAp, Ru content 5%) catalyst were purchased from Wako Pure Chemical Industries, Ltd. Poly(diallyldimethylammonium chloride) (PDADMAC, molecular weight ($M_W$): ca. $3 \times 10^5$; charge density (CD): 5.5 mequiv. $g^{-1}$ from Aldrich Ltd.) and anionic polyacrylamide HH-351 (A-PAM, $M_W$: ca. $4 \times 10^6$; CD: 0.83 mequiv. $g^{-1}$ from Kurita, Ltd.) were used as flocculants for handsheet-making with a dual polymer retention system.

### 2.2. Preparation of Ru sheet composite using a papermaking technique

Glass fiber (5.0 g) in 2 l deionized water was mixed with 100 ml of 4.95 mM aqueous $RuCl_3$ solution (Ru ca. 50.0 mg, 1 wt% on glass fiber) for 1 h. The resultant suspension was mixed with PDADMAC (0.05% on total solids) followed by the sequential addition of A-PAM (0.05% on total solids) at 3 min intervals. Subsequently, the mixture was poured into a pulp (0.5 g) suspension and handsheets with a size of 250 mm × 250 mm were prepared according to the appropriate TAPPI Test Method [16]. After pressing at 350 kPa for 5 min, the wet sheets were dried in an oven at 105 °C for 30 min. The thickness of Ru sheet was ca. 1 mm.

### 2.3. Selective oxidation of benzyl alcohol to benzaldehyde

The experiment was performed in batch mode as follows. The benzyl alcohol solution (1 mM, 3 ml) was prepared with acetonitrile and poured into a glass vessel. RuHAp powder (8 mg) or two pieces of Ru sheet (10 mm × 25 mm) with a Ru content of 0.4 mg was added to the reaction vessel. The reaction was carried out under static condition and the temperature of the reaction vessel was maintained at $30 \pm 1$ °C. After 1, 3, 6 or 24 h, the reaction solution (10 μL) was diluted with 90 μL of distilled water and was filtered with a membrane filter (Chromatodisk, pore size: 0.2 μm; GL Sciences, Ltd.). The diluted samples were examined by 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 gas chromatography–mass spectrometry (GC–MS) using 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).

### 2.4. X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis was performed with an AXIS-HSi spectrometer (Shimadzu/Kratos Co. Ltd.). The XPS spectra were obtained using a monochromatic Al Kα X-ray source (1486.6 eV) at a voltage of 15 kV and a current of 10 mA. The vacuum level of the analyzing chamber was maintained below $5 \times 10^{-7}$ Pa during the measurements. The pass energy and step width during the survey scan were set at 80 and 1 eV, respectively. In the C 1s, O 1s, Ru 3p, Ru 3d narrow scan mode, the scan parameters were set at 10 and 0.05 eV, respectively. The binding energies for all spectra were determined with respect to the C 1s reference signal (unoxidized C–C band) at 285.0 eV [17].

### 2.5. Other analyses

The ion-exchange behavior was evaluated by atomic absorption analysis; $Ru^{3+}$, $Na^+$, $Mg^{2+}$, $K^+$, $Ca^{2+}$ contained in the supernatant of the Ru-containing glass fiber suspension were quantified. Scanning electron microscopy (SEM) of the Ru sheet surface was performed with a JEOL JSM-5510 LV apparatus after platinum coating. The electron accelerating voltage was set at 6 kV.

## 3. Results and discussion

### 3.1. Preparation of Ru sheet by the papermaking technique

Fig. 1 shows optical and SEM images of an Ru sheet. The color of the glass fiber changed from white to gray after the Ru treatment and it is suggested that this is evidence that Ru was immobilized onto the glass fiber surface. $Ru^{3+}$ contained in the supernatant of suspension was below the detectable limit of atomic absorption analysis, thus nearly all of the Ru added to the system was immobilized onto the glass fibers. Ru-containing glass fibers were successfully fabricated into a sheet-shaped composite by an established papermaking technique employing a dual polymer retention system, whose mechanism was reported in our previous studies [8–13]. The Ru sheets consist of glass and pulp fiber, are flexible and have the external appearance of cardboard. Although the sheet strength of Ru sheet was lower compared to that of paper made only from pulp fibers, hydrogen bonds between pulp fibers mixed in the sheet improve the sheet strength enough to allow for handling in an organic solvent. From our SEM images, the appearance of the glass fiber was unchanged by Ru treatment and no accretion was observed at the glass fiber surface. Although the retention of Ru-containing glass fiber without using cationic and anionic polyelectrolyte was approximately 90%, the dual polymer retention system improved it up to nearly 100%.

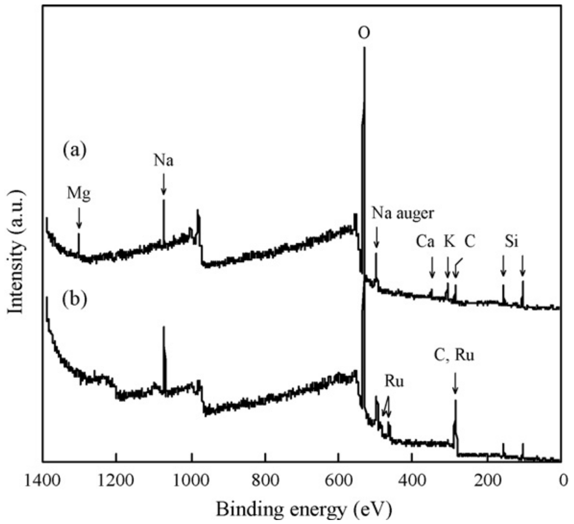

**Fig. 2.** XPS survey scan spectra of glass fiber sheet (a) and Ru sheet (b).

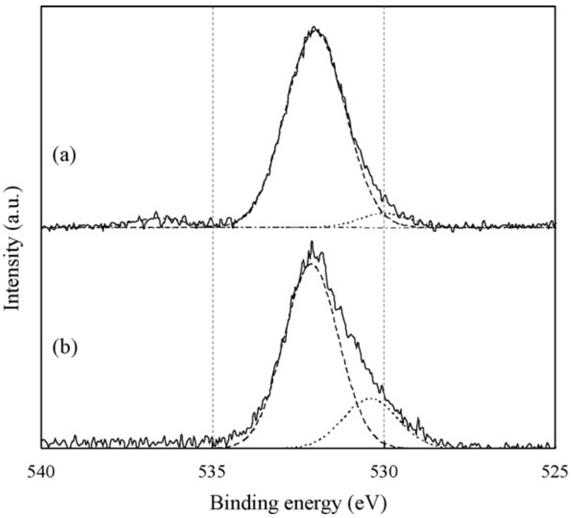

**Fig. 4.** O 1s narrow spectra of glass fiber sheet (a) and Ru sheet (b): peak derived from BO (dashed line), NBO (dotted line) and Na auger (dash-dotted line).

### 3.2. XPS analysis and ion-exchange behavior

Figs. 2 and 3 profile the XPS survey and Ru narrow spectra of the glass fiber sheet and the Ru sheet. In the XPS survey spectrum of the original glass fiber sheet, Na 1s, Mg 1s, K 2p and Ca 2p peaks were detected (Fig. 2a). In the case of Ru sheet, clear Ru $3p_{3/2}$ (462.8 eV) Ru $3p_{1/2}$ (485.5 eV) and Ru $3d_{5/2}$ (281.5 eV) peaks were detected (Fig. 3b) and indicated the presence of Ru on the glass fiber surface. It is likely that the appearance of a small C 1s peak at 285.0 eV originates from hydrocarbon contaminants. This peak is overlapped by the Ru $3d_{3/2}$ peak. However, Mg 1s, K 2p and Ca 2p peaks were not detected (Fig. 2b), thus it is suggested that Ru was introduced into glass fiber through ion-exchange.

O 1s narrow spectra of glass fiber sheets and Ru sheets are shown in Fig. 4 and it is clear that the O 1s peak is asymmetric. The oxygen atoms contained in the silicate glass were classified into bridging oxygen (BO: Si–O–Si) which composes the glass network and non-bridging oxygen (NBO: Si–O–R, where R is a cation) which locates at the end of the network and coordinates to cations. Fig. 5 displays the schematic illustration of the structure of glass. The two oxygen atoms give two individual peaks due to the different charge density [18–21]. According to previous studies, the O 1s narrow spectra of the original glass sheet and the Ru sheet were divided into two peaks and the peak with higher binding energy was attributed to BO (about 532.0 eV) and that with lower binding energy was attributed to NBO (about 530.0 eV) [18–21]. After Ru treatment, the

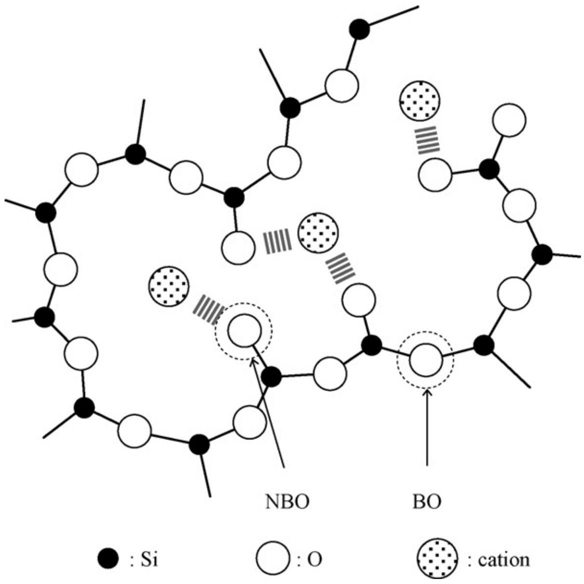

**Fig. 5.** Schematic illustration of the structure of glass.

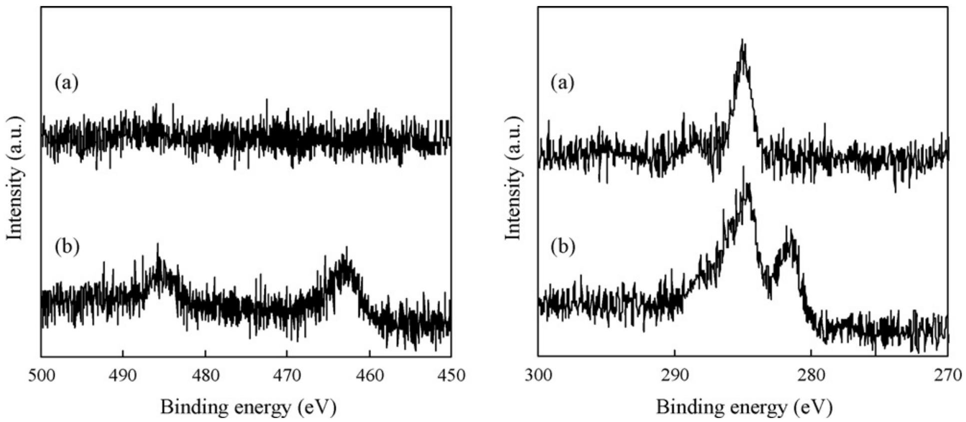

**Fig. 3.** Ru narrow spectra of glass fiber sheet (a) and Ru sheet (b).

**Table 1**
The amounts of cations contained in the supernatant of glass fiber suspension before and after Ru treatment.

| | Glass fiber suspension (μmol) | Glass fiber suspension after Ru treatment (μmol) | Cations leached through Ru treatment (μmol)[a] |
|---|---|---|---|
| $Na^+$ | 52.6 ± 3.6 | 90.4 ± 6.8 | 37.8 |
| $Mg^{2+}$ | 2.2 ± 0.2 | 5.2 ± 0.2 | 3.0 |
| $K^+$ | 4.4 ± 0.6 | 10.2 ± 0.8 | 5.8 |
| $Ca^{2+}$ | 3.6 ± 0.4 | 11.2 ± 0.4 | 7.6 |
| Total | 62.8 | 117.0 | 54.2 |

[a] Estimated values are obtained by subtracting the amount of cations contained in the glass fiber suspension from that after Ru treatment.

NBO peak shifted to higher value (530.5 eV) than that of the original glass fiber sheet, indicating that chemical state of NBO varied along with Ru immobilization. In the case of silicate glass, it has already been reported that the binding energy of NBO was affected by cation species contained in the glass structure and shifted to higher energy as the electronegativity of the coordinating cation increased, because charge density around NBO decreased: the binding energy of NBO of silicate glass with $Ag^+$ was higher than that of sodium silicate glass [18]. The electronegativity of Ru was also higher compared with that of Na, Mg, K and Ca, thus Ru coordinated to NBO and was immobilized, resulting in peak shift of NBO.

Table 1 shows the amount of cations existing in the supernatant of glass fiber suspension with and without Ru treatment. Although four cations leached from glass fibers into water without the treatment, the amounts of each cation increased through Ru treatment and the increase of cations contained in the supernatant corresponded well to the Ru added to the suspension (50.0 mg, 49.5 mol), thus the Ru immobilization mechanism seemed to be based on not simple surface adsorption but an ion-exchange mechanism. Once immobilized, no Ru leached from glass fibers. Yano et al. [18] suggested that metal ions having high electronegativity such as Ag would form covalent bonds with NBO. The interaction between Ru and NBO is strong enough to make a covalent bond because the electronegativity of Ru is higher than that of Ag, thus Ru is firmly immobilized onto the glass fiber surface.

### 3.3. Selective oxidation performance of Ru sheet

Selective oxidation of alcohols is an important chemical reaction and synthesized aldehydes serve as raw materials for various chemical products. Yamaguchi et al. [1] first reported the selective oxidation of alcohol by RuHAp and that primary alcohols may be converted to their corresponding aldehydes with a high degree of selectivity using molecular oxygen as a safe and inexpensive oxidant. Fig. 6 shows the variation with time of benzyl alcohol and benzaldehyde concentrations during selective oxidation when treated by Ru sheet and a commercial RuHAp powder. Both catalysts converted benzyl alcohol to benzaldehyde and the increase of benzaldehyde during the reactions corresponded to the decrease of benzyl alcohol. No noticeable amounts of intermediates were detected by HPLC or GC–MS analysis and therefore Ru immobilized onto glass fiber was able to oxidize benzyl alcohol to benzaldehyde selectively at 30 °C and under 1 atm air pressure. The oxidation mechanism for the use of Ru with molecular oxygen has previously been proposed in the literature; ligand exchange between benzyl alcohol and Ru and following β-hydride elimination occurred [3].

Ru sheet is better at selective oxidation of benzyl alcohol than RuHAp powder, although the same amount of Ru (0.4 mg) was used. Generally, the catalytic efficiency of molded or shaped catalysts is lower than powdery catalysts due to intra-particle diffusion limitations [22,23]. Recently, the influence of the macro-structure and properties of catalysts such as porosity and heat conductivity has become a major point of research interest and unique structure-independent effects on catalytic efficiency have been reported [22–24]. In our previous studies, porous catalyst sheets prepared by scattering catalyst powders on to fiber networks showed superior performance compared with standard catalyst powders and it was shown that the micron sized voids formed inside the sheets were significant for catalytic performance [10–13]. Within the sheets, the Ru seemed to be homogeneously scattered and immobilized onto the glass fiber surface and the porous nature of the sheet structure allows benzyl alcohol to pass inside the sheet through the voids and come into contact with the Ru, resulting in catalytic efficiency. From these results, it is clear that a sheet composite made of glass fiber is a highly suitable support for a metal catalyst and shows promise for future catalyst-based materials due to both practical convenience and catalytic performance.

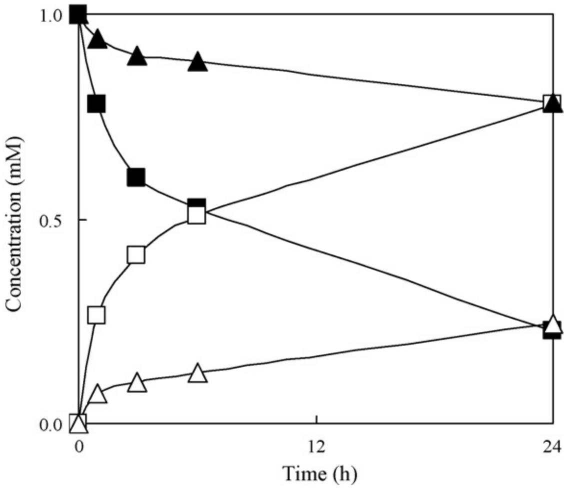

**Fig. 6.** Variation of benzyl alcohol (close) and benzaldehyde (open) concentrations with time for catalysis with Ru sheet (squares) and commercial RuHAp powder (triangles).

## 4. Conclusion

Ru-containing sheet composites were successfully prepared using ion-exchange techniques and an established wet papermaking method. These materials were successful applied to the selective oxidation of an alcohol. The porous Ru sheets were easily handled and strong enough to be used for reaction in an organic solvent. Ru was introduced into the glass structure by electrostatic interaction and became strongly attached onto the glass fiber surface.

The Ru sheet showed a higher alcohol conversion efficiency compared with a commercial Ru-containing catalyst powder in a batch reaction system. Ru sheets exhibit good catalytic efficiency compared with that obtained with a commercial catalyst because of the enhanced mass transfer provided by the presence of interconnected macropores that persist throughout the sheet-shaped composite. The sheet structure is adjustable to some extent by the wet papermaking process.

Ru sheet is a promising material, both in terms of practical application and catalytic performance.

## Acknowledgments

This research was supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. We thank Dr. Takuya Kitaoka, Dr. Shingo Yokota and Hirotaka Koga at Kyushu University for their help in XPS analysis.

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