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Immobilization of Ruthenium in Organic–Inorganic Hybrid Copolymers: A Reusable Heterogeneous Catalyst for Oxidation of Alcohols with Molecular Oxygen

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Dedicated to Professor Teruaki Mukaiyama on the occasion of his 80th birthday

Abstract: A novel organic–inorganic hybrid ruthenium (HB Ru) catalyst for the oxidation of alcohols with molecular oxygen has been developed. The catalyst was prepared from a polystyrene-based copolymer, which includes a trimethoxysilyl functionality, and dichlorotris(triphenylphosphine)ruthenium, $[RuCl_2(PPh_3)_3]$, as the metal source. A sol–gel process was employed for heterogenization of the catalyst. The choice of both ruthenium species and trialkoxysilyl-bearing monomers was found to be important for high catalytic activity. In the presence of HB Ru corresponding to 5 mol% loading of ruthenium, the alcohols were oxidized with molecular oxygen or air at atmospheric pressure without any additives to afford the corresponding aldehydes or ketones in good to excellent yields. The catalyst could be recovered and reused at least five times without loss of activity.

Keywords: heterogeneous catalysis · immobilization · oxidation · ruthenium · sol–gel processes

Introduction

The oxidation of alcohols to give aldehydes and ketones is one of the most important transformations in organic synthesis.[1] Whilst stoichiometric amounts of metal-based oxidants have been used for the oxidation, increasing environmental concerns have resulted in the development of catalytic reactions with green oxidants such as molecular oxygen.[2] Moreover, approaches toward heterogenization of catalytically active species onto solid supports are of benefit from a viewpoint of easy separation, recovery, and reuse of the catalysts.[3] Accordingly, a number of immobilized metal catalysts for aerobic oxidations have been intensely investigated in recent years, particularly well-studied are heterogeneous catalysts based on Pd,[4] Ru,[5] Au,[6] etc. and several multimetal systems[7].

We developed a novel metal-catalyst-immobilization technique, the polymer incarceration (PI) method based on microencapsulation and cross-linking.[8] Recently, we reported two PI metal catalysts, PI Ru[5m] and PI Au[6c], for oxidation of alcohols with molecular oxygen to afford the corresponding aldehydes and ketones, and found that these catalysts could be recovered and reused at least ten times. PI Ru was successfully applied to the oxidation of various alcohols, including a primary aliphatic alcohol. However, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) was required as co-oxidant to achieve high catalytic activity, and the leaching of Ru metal was observed in some cases (never exceeded 0.72%). Efficient heterogeneous catalysts with no metal leaching and that operate without additives are highly desirable owing to simple product purification and a decrease in chemical waste.

Heterogeneous catalysts have often been prepared, without loss of their structure around the active center, by immobilization of the catalytically active species through covalent bonding to polymer resins.[9] Although polymer-supported catalysts retain some of their homogeneous nature and may be easily modified, they suffer from a lack of chemical and/or mechanical resistance, resulting in metal leaching.

A solution to these problems would be the introduction of inorganic species to organic moieties to create organic–inorganic hybrid catalysts.[10] Generally, the sol–gel approach

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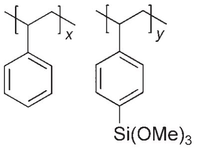
is used to prepare the catalysts; that is, hydrolysis of trialkoxysilane and subsequent polycondensation to make insoluble catalysts for various solvents. Although numerous efforts have been made in this field, only a few additive-free catalyst systems have been reported for the aerobic oxidation of alcohols and oxidant-free dehydrogenation of alcohols.[5i,j,11] Pagliaro and co-workers reported recyclable catalysts for aerobic oxidation of alcohols that are prepared from organically modified silicates doped with tetra-*n*-propylammonium perruthenate (TPAP).[5i,j] The catalyst was entrapped in the extensive internal pores of porous oxides. As an alternative hybridization strategy we decided to introduce a trialkoxysilyl group through chemical bonding into our polymer support previously developed to create an organic–inorganic hybrid network. This approach would make it possible to modify the polymer structures by varying inorganic species. Therefore, hydrophobicity/hydrophilicity and chemical/mechanical resistance of the hybrid catalysts could be controlled.

Herein we describe a novel organic–inorganic hybrid ruthenium catalyst prepared from a polystyrene-based copolymer containing a trialkoxysilyl functionality by microencapuslation of a ruthenium source followed by cross-linking. The heterogeneous catalyst thus prepared showed high activity for the oxidation of alcohols with molecular oxygen.

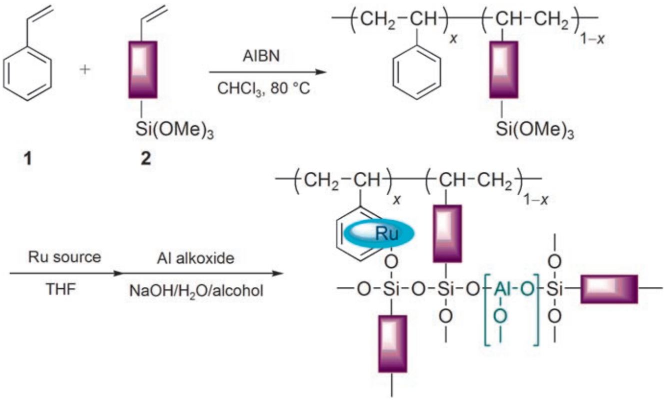
Results and Discussion

The preparation of copolymer was investigated by free radical copolymerization of styrene with one of three monomers, which are readily available: allyltriethoxysilane, 3-(trimethoxysilyl)propyl methacrylate, and *p*-styryltrimethoxysilane. When allytriethoxysilane was used as a component, only styrene was polymerized; presumably dπ–pπ interactions between the Si atom and the olefin decrease the propensity for polymerization.[12] 3-(Trimethoxysilyl)propyl methacrylate and *p*-styryltrimethoxysilane were successfully polymerized with styrene. The copolymers thus prepared were dissolved in THF at room temperature, and a ruthenium source and an aluminum alkoxide were then added. To this solution, a mixture of aqueous NaOH (1 N) and an alcohol were added quickly to initiate the sol–gel process. The suspension was heated gradually to 120 °C to remove the solvent, and a black solid remained. Scheme 1 illustrates the synthesis of the hybrid ruthenium catalyst.

It was found that the addition of aqueous NaOH was essential to obtain high catalytic activity and selectivity. We selected *p*-styryltrimethoxysilane as a trialkoxysilane-bearing monomer because the catalyst prepared from 3-(trimethoxysilyl)propyl methacrylate might be unstable during the catalyst preparation owing to cleavage of the ester moiety. Finally, the copolymer $\mathbf{P_0}$ was used in the catalyst preparation to give an organic–inorganic hybrid catalyst.

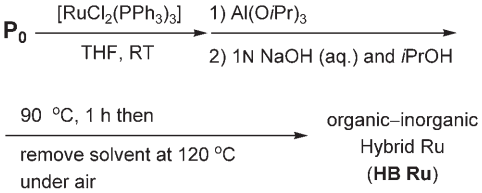


$\mathbf{P_0}$ (*x*/*y* 80:20)



Scheme 1. General synthetic pathway for organic-inorganic hybrid catalysts.

Dichlorotris(triphenylphosphine)ruthenium $[RuCl_2(PPh_3)_3]$ and ruthenium chloride hydrate $RuCl_3{\cdot}n\,H_2O$ were screened as potential catalytic metal sources. $[RuCl_2(PPh_3)_3]$ was the most suitable for heterogenization by the sol–gel method, because hydrolysis of the trimethoxysilyl group occurred before the addition of aqueous NaOH in the case of $RuCl_3{\cdot}n\,H_2O$, presumably because of its high Lewis acidity. After optimization of several parameters to give the organic–inorganic hybrid ruthenium (HB Ru), we finally found that the preparation method shown in Scheme 2 gave the best catalytic performance in the oxidation of alcohols with molecular oxygen at atmospheric pressure.



Scheme 2. Preparation of organic-inorganic hybrid ruthenium (HB Ru).

The scope of the aerobic oxidation of alcohols with the HB Ru system was studied with alcohols bearing heteroatoms and benzylic, aliphatic, and allylic groups (Table 1). Benzyl alcohol derivatives were oxidized to the corresponding aldehydes in excellent yields (Table 1, entries 1–8). We examined the oxidation of 4-methoxybenzyl alcohol with air at atmospheric pressure instead of molecular oxygen, and no decrease in catalytic activity was observed. 2-Methylbenzyl alcohol was also successfully converted into 2-methylbenzaldehyde by using the HB Ru system (Table 1, entries 6, 7). In other catalytic systems, the low conversion of 2-substituted benzyl alcohols was proposed to be due to steric hindrance of the quasi-two-dimensional surface of the nanoparticles.[4f,13] 1-Naphthalenemethanol and cinnamyl alcohol also underwent smooth oxidation under the same conditions (Table 1, entries 9 and 10). HB Ru was also found to be applicable to the oxidation of heterocyclic alcohols, in-

Table 1. Oxidation of various alcohols catalyzed by HB Ru.[a]

$$\text{Substrate} \xrightarrow[\text{Toluene}]{\text{O}_2\ (0.1\ \text{MPa}),\ \textbf{HB Ru}\ (5\ \text{mol\%})} \text{Product}$$

Entry	Substrate	T [°C]	t [h]	Conv. [%][b]	Yield [%][b]
1	4-methoxybenzyl alcohol	110	2	>99	92
2	4-methoxybenzyl alcohol	90	2	>99	92
3[c]	4-methoxybenzyl alcohol	90	2	>99	94
4	4-methylbenzyl alcohol	110	2	>99	97
5	benzyl alcohol	110	3	>99	97
6	2-methylbenzyl alcohol	90	3	>99	90
7	2-methylbenzyl alcohol	70	12	96	94
8	4-chlorobenzyl alcohol	110	6	>99	93
9	1-naphthalenemethanol	110	7	>99	93
10	cinnamyl alcohol	110	10	>99	92
11	2-thiophenemethanol	90	4	>99	95
12	furfuryl alcohol	110	18	>99	82
13	furfuryl alcohol	90	16	97	85
14	1-decanol	110	24	77	35
15[d]	1-decanol	90	10	70	20
16[d]	3-phenyl-1-propanol	110	40	72	36
17	(±)-1-phenylethanol	110	9	>99	98
18	1-(2-thienyl)ethanol	110	14	>99	>99
19	2-adamantanol	110	18	>99	92
20	cyclohexanol	110	48	22	13
21	cyclooctanol	110	48	37	31
22[d]	cyclooctanol	110	48	56	44
23[d]	2-octanol	110	48	77	68

[a] Unless otherwise stated, the reactions were carried out with the alcohol (0.4 mmol) under O_2 at atmospheric pressure. [b] Determined by GC analysis. [c] Under air instead of O_2. [d] HB Ru: 10 mol%.

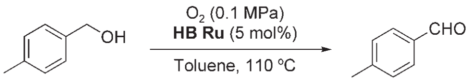
cluding sulfur atoms (Table 1, entries 11, 18). On the other hand, the oxygen-containing heterocycle furfuryl alcohol gave a slightly lower yield (Table 1, entries 12, 13), and the oxidation of primary aliphatic alcohols was also found to proceed in lower yields (Table 1, entries 14–16). The secondary alcohol (±)-1-phenylethanol was also oxidized to afford the corresponding ketone in 98% yield (Table 1, entry 17). In the oxidation of an aliphatic secondary alcohol to the corresponding ketone, for example, 2-adamantanone was obtained in 92% yield (Table 1, entry 19), whereas cyclohexanol (Table 1, entry 20) and cyclooctanol (Table 1, entries 21, 22) were found to be less reactive under these conditions. On the other hand, 2-octanol was converted into the corresponding ketone in moderate yield (Table 1, entry 23).

Induced coupled plasma (ICP) analysis was used to detect Ru in the filtrate, and it was found that the leaching level was below 0.010% in all cases, except for some primary aliphatic alcohols with longer reaction times during which a small amount of Ru leaching was detected (Table 1, entries 14 (0.93%) and 16 (0.94%)).

The catalyst was recovered by simple filtration and reused (Table 2). After the recovery of the catalyst and treatment with aqueous K_2CO_3 (1 M), it could be reused at least five times without loss of activity (Table 2, entry 2).

Some characterization methods were applied to obtain the structural information of HB Ru. No chlorine atoms (<0.1 wt%) were detected by flask combustion-ion chromatography, and only a small amount of phosphorous atoms (0.3 wt%) was detected by ICP analysis. It was revealed by ^{31}P SR-MAS (swollen-resin magic-angle-spinning) NMR spectroscopy[14] that a single peak of the phosphine oxides on HB Ru was observed. We also conducted transmission electron microscopy (TEM) analysis (Figure 1). The catalyst appears to be uniform and consists of both organic and inorganic parts. The specific surface area of the catalyst was determined to be $6.0\ \text{m}^2\,\text{g}^{-1}$ by the Brunauer–Emmett–Teller (BET) method at −196 °C. Notably, high catalytic activity with relatively narrow surface area is one of characteristic points of PI catalysts. Further, to evaluate the actual weight ratio of the polymer and inorganic species in HB Ru, ther-

Table 2. Recovery and reuse of HB Ru.[a]



Entry	Treatment	1st (%)	2nd (%)	3rd (%)	4th (%)	5th (%)
1	none	97 (3)	67 (7)	-	-	-
2	1 M K_2CO_3 aq.	97 (3)	95 (3)	95 (3)	95 (3)	95 (3)

[a] Yields were determined by GC analysis. The values shown in parentheses were reaction times (h).

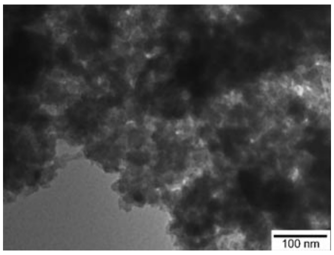


Figure 1. TEM image of HB Ru.

mal gravimetric analysis (TGA) was performed under air from room temperature to 1000 °C. As the weight loss at 993 °C was 68 %, which indicates polymer decomposition, HB Ru was found to contain 32 % inorganic species.

Conclusions

In summary, a novel organic–inorganic hybrid ruthenium catalyst (HB Ru) for the oxidation of alcohols with molecular oxygen was developed. This catalyst was prepared from $[RuCl_2(PPh_3)_3]$ as metal source and copolymer $\mathbf{P_0}$, which has a trimethoxysilyl functionality for the heterogenization of the catalyst. The sol–gel process was initiated by the addition of aqueous NaOH, followed by polycondensation (cross-linking) to afford the heterogeneous organic–inorganic hybrid ruthenium catalyst. The oxidation of various alcohols proceeded smoothly to give the corresponding aldehydes and ketones in good to excellent yields. Moreover, it was found that no leaching of Ru was observed in almost all cases. The recovered catalyst could be treated with aqueous K_2CO_3 (1 M) to facilitate its reuse. Further investigations to apply this novel system to the immobilization of other transition metals are in progress.

Experimental Section

General Remarks

The formation of oxidized compounds (aldehydes and ketones) was confirmed by comparison with commercially available compounds by gas chromatographic (GC) analysis (60 m × 0.25 mm DB-1 column for aldehydes, 60 m × 0.25 mm TC-WAX column for ketones).

Preparation of copolymer (P_0)

Styrene (7.50 g, 72.0 mmol), *p*-styryltrimethoxysilane (4.04 g, 18.0 mmol), and AIBN (148 mg, 0.90 mmol) were mixed in chloroform (12.0 mL). The mixture was stirred for 24 h at 80 °C and then cooled to room temperature. The resulting polymer solution was poured slowly into hexane. After the crude copolymer was precipitated and the liquid removed, the obtained solid was dissolved in dichloromethane. The solution was poured slowly into hexane, and the same procedure repeated twice. The purified copolymer was filtered, washed with hexane several times, and dried (12 h at room temperature in vacuo) to afford the desired copolymer $\mathbf{P_0}$ (9.97 g, 86 % yield). The molar ratio of the component was determined by ^{1}H NMR spectroscopic analysis (x/y 80:20). M_w, M_n, and M_w/M_n ratio were measured by gel-permeation chromatography (GPC) based on standard polystyrene calibration ($M_w = 14500$, $M_n = 7460$, $M_w/M_n = 1.95$).

Preparation of HB Ru:

Copolymer $\mathbf{P_0}$ (1.00 g) was dissolved in THF (22.5 mL) at room temperature. $[RuCl_2(PPh_3)_3]$ (1.00 g, 1.04 mmol) was added to this solution, and the mixture was stirred for 3 h at this temperature. $Al(OiPr)_3$ (213 mg, 1.04 mmol) was then added, and the mixture was stirred for 1 h at room temperature. A mixture of aqueous NaOH (1.0 N, 5.0 mL) and *i*PrOH (5.0 mL) was then added quickly, and the mixture was stirred for 11 h at room temperature. The resultant suspension was heated at 90 °C for 1 h, and gradually heated to 120 °C to remove the solvent. The resultant solid was washed with THF, MeOH, water, acetone, and dichloromethane several times and dried in vacuo for 5 h to give organic–inorganic hybrid ruthenium (HB Ru, 1.15 g). The ruthenium metal loading was determined by ICP analysis (0.649 mmol g^{-1}).

Typical Procedure for Oxidation of Alcohols Catalyzed by HB Ru

(Table 1): 4-Methylbenzyl alcohol (0.40 mmol) and HB Ru (0.649 mmol g^{-1}, 5 mol %) were combined in toluene (1.6 mL), and the mixture was stirred for 2 h under O_2 (0.1 MPa) at 110 °C. Hexane was then added to quench the reaction, and the catalyst was collected by filtration and washed with dichloromethane. The yield of 4-methylbenzaldehyde was determined by GC analysis (naphthalene as internal standard). Metal leaching was determined as follows: After determination of the yield of the reaction, the filtrate was filtered again through celite to remove fine particles. The solvents were removed in vacuo, and concentrated sulfuric acid (1.0 mL) was added to the residue. This suspension was heated at 180 °C for 2 h, and then a few drops of nitric acid were added to dissolve the insoluble materials, the mixture was kept at the same temperature for 1 h. The Ru content of the obtained solution was determined by ICP analysis.

Recovery and Reuse of HB Ru

(Table 2): 4-Methylbenzyl alcohol (122 mg, 1 mmol) and HB Ru (0.626 mmol g^{-1}, 5 mol %) were combined in toluene (4 mL), and the mixture was stirred for 3 h under O_2 (0.1 MPa) at 110 °C. Hexane was then added to quench the reaction, and the catalyst was collected by filtration and washed with dichloromethane. The yield of 4-methylbenzaldehyde was determined by GC analysis (naphthalene as internal standard). The filtered catalysts was then dried in vacuo, aqueous K_2CO_3 (1 M, 1 mL), THF (3 mL), and MeOH (3 mL) were added, and the mixture was stirred for 1 h at 60 °C. The catalyst was collected by filtration and washed with dichloromethane again, then dried and reused.

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