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Synthesis of a polymer–ruthenium complex Ru(pbbp)(pydic) and its catalysis in the oxidation of secondary alcohols with TBHP as oxidant

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Abstract A polymer–ruthenium complex Ru(pbbp)(pydic) was synthesized from the reaction of poly-2,6-bis(benzimidazolyl)pyridine (pbbp) with $RuCl_3$ and disodium pyridine-2,6-dicarboxylate (pydic). The Ru(pbbp)(pydic) was characterized thoroughly by spectroscopic methods. ICP analysis revealed that the percentage of complexation of 2,6-bis(benzimidazolyl)pyridine unit in pbbp was about 83%. The complex was tested as a heterogeneous catalyst for the oxidation of secondary alcohols to their corresponding carbonyl compounds in solvent-free conditions using aqueous *tert*-butyl hydroperoxide as oxidant. The developed catalytic system exhibited high activity and broad functional group compatibility, allowing a variety of secondary alcohols, including substituted secondary benzylic alcohols and secondary aliphatic ones, to be oxidized to the corresponding ketones in high yields. This Ru(pbbp)(pydic) could be recycled for several times, but it dissolved in part in the reaction mixture during the catalytic run leading to gradual deactivation of the catalyst with repeated runs.

Introduction

Oxidation of alcohols to the corresponding carbonyl compounds is of great importance both in academia and in industry [1–3]. Traditional methods to perform this reaction involve the use of stoichiometric or even over-stoichiometric chromium(VI) oxide [4–7], MnO_2 or hypervalent iodine compounds [8–13] as oxidants, which can generate large amounts of waste and cause environmental problems. Therefore, it is crucial to develop cleaner catalytic oxidation systems to realize the oxidation processes. From the viewpoints of both economy and environmental protection, the use of molecular oxygen as the terminal oxidant is most promising, because molecular oxygen is widely available and only water as byproduct is formed in the reaction in principle. For this purpose, many catalytic systems have been developed, and the ones based on stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) with various transition metal salts as co-catalysts are the most reported [14–17]. However, the catalytic systems developed using molecular oxygen as terminal oxidant only showed high efficiency in the oxidation of primary alcohols, and unfavorable results were generally received in the cases of secondary alcohols as substrates. Therefore, it is essential to contrive protocols to convert secondary alcohols to the corresponding ketones.

Generally, hydrogen peroxide (H_2O_2) and TBHP are also considered to be environmentally benign oxidants, though they are slightly inferior compared to molecular oxygen. Various transition metals or their complexes were found to be efficient in the oxidation of secondary alcohols to the corresponding ketones with H_2O_2 or TBHP as oxidant [18–23]. Among the transition metal complexes, several Ru complexes showed excellent performances in the reaction [24–27]. For instance, Ru(terpyridine)(2,6-pyridinedicarboxylate) [hereafter abbreviated as Ru(terpy)(pydic)] performed very well in the oxidation of secondary alcohols to the ketones with H_2O_2 as oxidant in the absence of any co-catalysts or organic solvents [24]. Another ruthenium complex termed ruthenium-bis(benzimidazole)(pyridinedicarboxylate) also showed high

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efficiency in oxidation reactions with H_2O_2 as the oxidant [25]. Very recently, an *N*,*N*,*N*-tridentate ligand Ru complex—Ru(pymieb)(pydic) designed and synthesized by us exhibited excellent activity in the oxidation of various secondary alcohols to the ketones with TBHP as oxidant under mild and solvent-free conditions [26]. In spite of the excellent performances of these ruthenium complexes in the reaction, it is very difficult to separate the expensive complexes from the reaction mixture, making them impossible to recycle. Heterogenization of the ruthenium complexes was used to overcome this difficulty. For instance, a silica gel immobilized $[(Me_3\text{-}tacn)Ru^{III}(CF_3COO)_2(H_2O)]CF_3CO_2$ complex (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) prepared by Che et al. showed high activity and good recyclability in the oxidation of secondary alcohols to the ketones with TBHP as oxidant [27]. Recently, we successfully immobilized Ru(terpy)(pydic) onto MCM-41 using a multi-step grafting method [28]. This immobilized ruthenium complex exhibited excellent performance in the oxidation of various secondary alcohols to the corresponding ketones with TBHP as oxidant and had the advantages of easy recovery and good reusability, too. Though the heterogenization of the complexes received promising results, the immobilization processes were generally complicated. It was reported that a polymer containing the tridentate 2,6-bis(benzimidazol-2-yl)pyridine moiety was easily synthesized by the condensation reaction between pyridine-2,6-dicarboxylic acid and 3,3′-diaminobenzidine tetrahydrochloride dihydrate in the presence of polyphosphoric acid, and this polymer can coordinate with ruthenium to give polymer–metal complexes exhibiting good thermal stabilities [29]. Inspired by this report, we have used this polymer in combination with pydic coordinating with $RuCl_3$ to form a polymer–metal complex with a Ru[bis(benzimidazol-2-yl)pyridine](2,6-pyridinedicarboxylate) moiety. The resulting polymer–ruthenium complex Ru(pbbp)(pydic) was applied to the oxidation of secondary alcohols with TBHP as oxidant. The catalytic results showed that the complex has good activity and could be recycled several times in the reaction.

Experimental

Reagents and apparatus

All the reagents and solvents were purchased from commercial sources and used as received without further purification. 3,3′-Diaminobenzidine tetrahydrochloride dehydrate (98%) was purchased from Source Leaf Biological Technology Co., Ltd. $RuCl_3\cdot 3H_2O$ was supplied by Xi'an Kaili Chemical Company. Pyridine-2,6-dicarboxylic acid (98%) and TBHP (70%) were purchased from Energy Chemical, China. H_2O_2 (30%) and all solvents, AR grade, were obtained from Tianjin Guangfu Fine Chemical Research Institute. The ligand pydic was prepared by treatment of pyridine-2,6-dicarboxylic acid with sodium hydroxide. The alcohols were obtained from Alfa Aesar China (Tianjin) Co., Ltd.

^1H NMR spectra were measured in DMSO-d_6 and $CDCl_3$ on a Bruker AC-P 400 spectrometer with tetramethylsilane as an internal standard. The metal content of the catalyst samples was analyzed using a PerkinElmer Opfima 7300V type ICP-AES instrument. Before analysis, the accurately weighed sample was carefully added into a flask, and then nitric acid and perchloric acid were added. The suspension was heated to dissolve the sample, and the obtained solution was subjected to analysis. FTIR spectra were recorded on a Bruker Vector 22 instrument in the wave number range of 400–4000 cm^{-1} with the samples in the form of KBr pellets. UV–Vis spectra were collected in the range of 200–800 nm on a Varian Cary 300 UV–visible spectrophotometer. Thermogravimetric analysis of the pbbp and Ru(pbbp)(pydic) was performed on an SDT/Q600 thermogravimetric analyzer at a temperature range of 20–1200 °C with a temperature ramp of 10 °C/min under an air environment. Scanning electron microscopy (SEM) was carried out with a Nova Nano SEM450 instrument and an Octane Pro Det. Oxidation reaction samples were analyzed by a Shandong Lunan Ruihong Gas Chromatograph (SP-7800A) equipped with an FID detector and an SE 54 column (30 m × 0.5 μm).

Catalyst preparation

Synthesis of pbbp

3,3′-Diaminobenzidine tetrahydrochloride dihydrate (1.98 g, 5 mmol) was gradually added to freshly prepared PPA (50 g, 85% P_2O_5) under nitrogen atmosphere at about 80 °C. After eliminating the hydrochloride, pyridine-2,6-dicarboxylic acid (0.83 g, 5 mmol) was added into the solution. The resulting slurry was maintained at 150 °C for about 24 h and then at 200 °C for 30 h, respectively. The viscous polymer solution was poured into hot water, and the mixture was stirred vigorously for 1 h in order to eliminate any residual of monomer and PPA. The solid was filtered off and washed with aqueous sodium hydroxide solution (5%). Then it was washed with water till the pH of the filtrate reached 7. The solid was then purified by washing with water in a Soxhlet extractor and finally dried under vacuum for 24 h (1.21 g, yield 78%). ^1H NMR (400 MHz, DMSO-d_6, TMS) δ(ppm): 7.70–7.77(m, 2H), 7.79–7.94(m, 2H), 8.07–8.25(m, 3H), 8.38–8.44(m, 2H), 13.11–13.21(br, 2H). IR(KBr, cm^{-1}) ν: 3407, 1626, 1596, 1562, 1437, 1304, 992, 803. UV/Vis (DMF) λ_{max} = 266, 357 nm.

Synthesis of Ru(pbbp)(pydic)

To a solution of $RuCl_3{\cdot}3H_2O$ (131 mg, 0.5 mmol) in MeOH (8 ml) was added a solution of pydic (156 mg, 0.5 mmol) in MeOH–H_2O (2:1, 12 ml) under nitrogen atmosphere. The mixture was heated and refluxed for 1 h and then cooled to room temperature. The solvent was evaporated under vacuum. The residue was dissolved in DMF (200 ml), and pbbp (150 mg, 0.5 mmol, calculated from the molecular weight of the repeating unit) was added to the above DMF solution under stirring. The mixture was heated at 100 °C for 24 h under nitrogen atmosphere. The mixture became homogeneous during the course of the reaction. The reaction mixture was cooled to room temperature and poured into diethyl ether (150 ml). A dark green precipitate was formed and collected by suction filtration. The product was washed thoroughly with methanol and was collected as a dark green solid (0.23 g, yield 82%). The ruthenium content of the catalyst was analyzed using ICP and was found to be 14.5%. IR (KBr, cm^{-1}) ν: 3400, 1620, 1564, 1450, 1386, 1308, 1150, 1020, 803, 472. UV/Vis (DMF) $\lambda_{max} = 264, 360, 586$ nm.

Catalytic oxidation of alcohols

In a typical process, into a 5-ml two-necked round-bottom flask equipped with a magnetic stirrer were added Ru(pbbp)(pydic) (0.002 mmol) and alcohol (2 mmol) successively at room temperature. The mixture was heated to 60 °C under stirring, and then TBHP (70% aqueous solution) was slowly dropped in 0.5 h. The reaction was monitored by GC equipped with a SE 54 column (30 m × 0.5 μm). After reaction, the product was purified by column chromatography over silica gel (eluent: *n*-hexane/ethyl acetate) and characterized by ^1H NMR.

Results and discussion

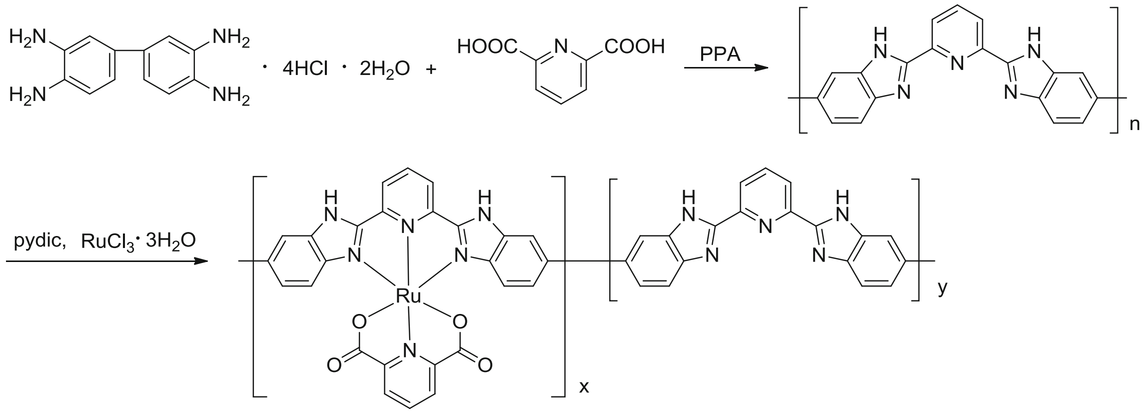
Synthesis of Ru(pbbp)(pydic)

The synthesis route of the Ru(pbbp)(pydic) is shown in Scheme 1. The polymer pbbp was prepared as described in the literature [29]. The condensation reaction between 3,3′-diaminobenzidine tetrahydrochloride dihydrate and pyridine-2,6-dicarboxylic acid smoothly afforded pbbp in high yield in the presence of PPA as the reaction medium. The physical properties of the solid product including solubility in organic acids such as methanesulfonic acid, formic acid, trifluoroacetic acid and ^1H NMR are identical with the literature report [29].

It was reported that substituted terpyridine or 2,6-bis(benzimidazolyl)pyridine in combination with pydic can coordinate with $RuCl_3$ to afford the corresponding Ru(L)(pydic) complex (L = BINOL-terpyridine or 2,6-bis(*N*-octadecylbenzimidazol-2-yl)pyridine) [30, 31]. Therefore, $RuCl_3$ was employed as the ruthenium source to prepare the polymer–ruthenium complex Ru(pbbp)(pydic). Pre-coordination of pydic with $RuCl_3$ was required to facilitate the dissolution of pydic in DMF. The Ru(pbbp)(pydic) was synthesized by heating a mixture of pbbp with $RuCl_3$–pydic in DMF at 100 °C in high yield. Ru(pbbp)(pydic) has much higher solubility in DMF than pbbp. The enhancement in solubility in coordination of pbbp with ruthenium in polar aprotic solvent was also observed in other ruthenium–polymer complexes [29]. The ruthenium content determined by ICP was 14.5%, from which it can be estimated that the percentage of complexation was about 83%, or the ratio of x to y in Scheme 1 was 83:17.

Characterization

The Ru(pbbp)(pydic) was firstly characterized by FTIR, and the spectra of the complex and pbbp are shown in



Scheme 1 Synthesis route for Ru(pbbp)(pydic)

Fig. 1. The absorption band at 1626 cm^{-1} in the spectrum of pbbp (a) is assigned to the C=N stretching in the imidazole, and the bands at 1596 and 1562 cm^{-1} are assigned to the C=N stretching vibration of the pyridine ring [29]. Compared with that of pbbp, the spectrum of Ru(pbbp)(pydic) (b) exhibits an additional band at 1620 cm^{-1}, attributed to the C=O stretching in the pydic [25], and a weak band at 472 cm^{-1} attributed to Ru–N vibration [32]. Besides, all the characteristic peaks in the spectrum of ruthenium-bis(benzimidazole)pyridinedicarboxylate complex [Ru(bbp)(pydic)] [25] can be found in that of Ru(pbbp)(pydic). These results indicate the formation of the Ru(pbbp)(pydic).

The electronic spectra for dilute solutions of pbbp and Ru(pbbp)(pydic) in DMF (2.5×10^{-5} M) are shown in Fig. 2. In the spectrum of pbbp (a), the bands maxima at 266 and 357 nm are, respectively, derived from the π–π* transitions of phenyl and C=N groups [29, 33]. After the formation of Ru(pbbp)(pydic) (b), an additional weak absorption band at 586 nm is observed, it is assigned to the metal–ligand charge transfer [MLCT, d(Ru) → π*(pyridine)] transition, which is a characteristic transition band in ruthenium polypyridine complexes [29, 34].

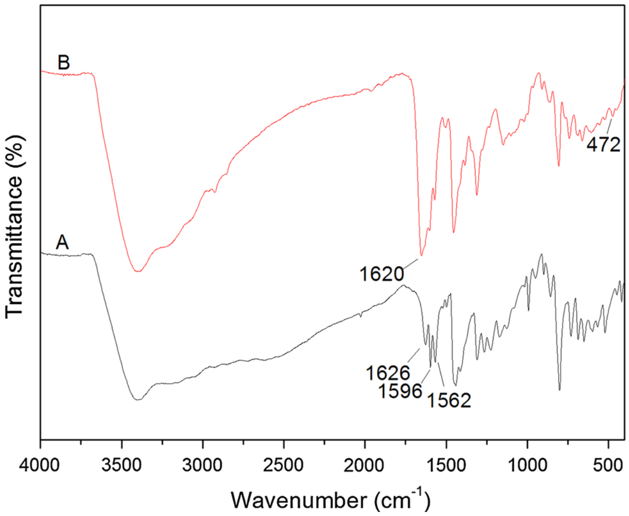


Fig. 1 FTIR spectra of pbbp (*a*) and Ru(pbbp)(pydic) (*b*)

The thermal stability of pbbp and Ru(pbbp)(pydic) was investigated by thermogravimetric analysis (TGA). Figures 3 and 4 show the TG and DSC curves for pbbp and Ru(pbbp)(pydic), respectively. As shown in Figs. 3 and 4, both the samples of pbbp and Ru(pbbp)(pydic) show an initial endothermic stage occurring in the range of 50–150 °C, with a weight loss of 10%, being ascribed to the desorption of physisorbed water. In Fig. 3, the second weight loss beginning at about 530 °C is due to the exothermic oxidative decomposition of pbbp [29]. In Fig. 4, the second stage between 300 and 450 °C is corresponding to the exothermic oxidative degradation of the complex. A weight loss of 65% takes place in this stage. Therefore, we can conclude that Ru(pbbp)(pydic) is stable when it is employed as catalyst below 300 °C.

The samples of pbbp (a), fresh Ru(pbbp)(pydic) (b), Ru(pbbp)(pydic) after the first run (c) and the third run (d) were analyzed using SEM, and the results are presented in Fig. 5. The SEM images show that the sample of pbbp consists of irregular mass particles, and the samples of fresh and used Ru(pbbp)(pydic) retain nearly the same morphology to that of the pbbp. Part fragmentation of Ru(pbbp)(pydic) was found in the catalytic runs by comparing the images of the used samples with that of the fresh one.

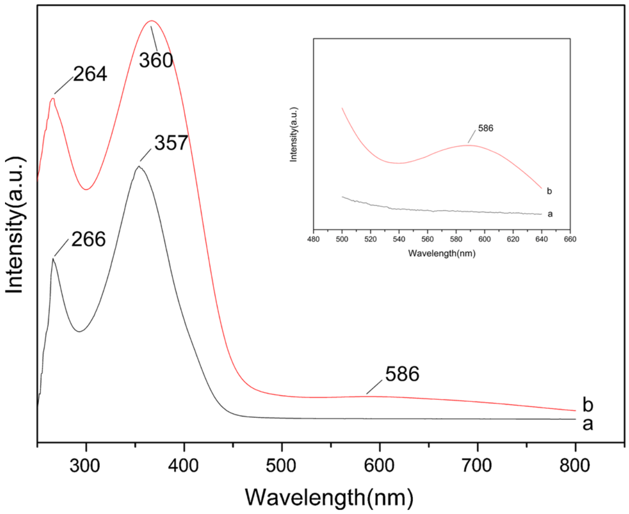


Fig. 2 UV–Vis spectra of pbbp (*a*) and Ru(pbbp)(pydic) (*b*)

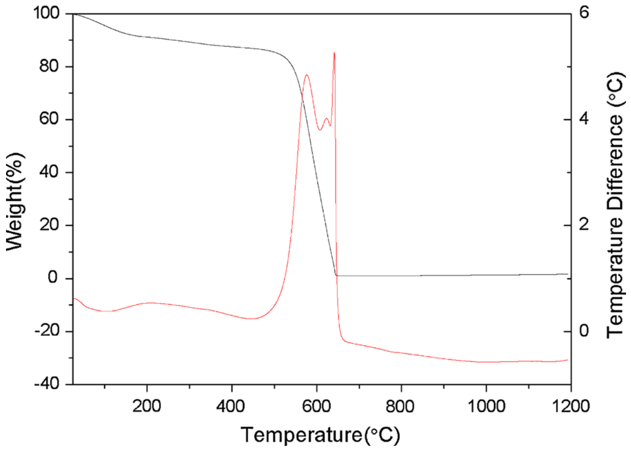


Fig. 3 TG and DSC curves of the thermal degradation of pbbp

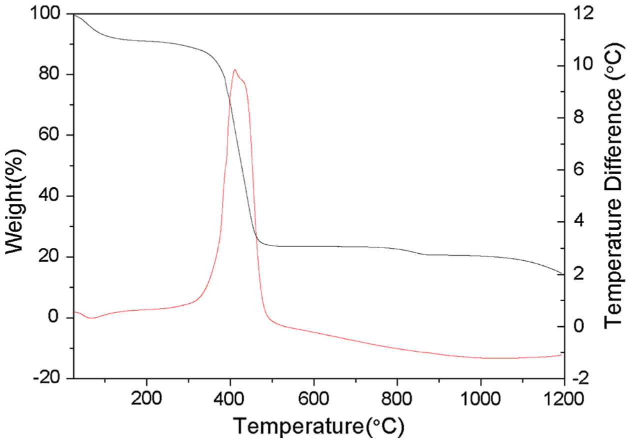


Fig. 4 TG and DSC curves of the thermal degradation of Ru(pbbp)(pydic)

Catalytic activity

The Ru(pbbp)(pydic) was employed as a catalyst in the oxidation of secondary alcohols to the corresponding ketones. First, the catalytic performance of Ru(pbbp)(pydic) in the reaction was evaluated using 1-phenylethanol as a model substrate. Initially, various oxidants including O_2, H_2O_2, TBHP were screened in the reaction under solvent-free conditions. As shown in Table 1, almost no reaction took place in the case of oxygen as oxidant (Table 1, entry 1). Unexpectedly, low conversion was obtained in the case of 30% aqueous H_2O_2 as oxidant (Table 1, entry 2), which is very different from that catalyzed by the corresponding complex Ru(terpy)(pydic) [24]. To our delight, TBHP showed good performance in the reaction and the conversion of 1-phenylethanol reached up to 99% with a selectivity of 99% toward acetophenone in 4 h at 40 °C (Table 1, entry 7). The catalytic reaction was also carried out in different solvents. However, the reaction proceeded slowly, and only moderate conversions of 1-phenylethanol were obtained in more than 5 h in the solvents tested (Table 1, entries 3–6).

The parameters influencing the reaction were optimized under solvent-free conditions. First, the effect of reaction temperature on the reaction was examined, and the results are listed in Table 2. From the table, we can find that it took 15 h to finish the reaction when it was conducted at 25 °C (Table 2, entry 1). Increasing temperature can accelerate the reaction (Table 2, entries 2–4), and the reaction time to completion was only 2 h at 60 °C (Table 2, entry 3). Further increasing temperature can still increase the reaction rate, but it may cause safety problems in large-scale application of TBHP. Therefore, 60 °C was selected as the reaction temperature in the subsequent experiments.

The catalyst loading was optimized at 60 °C keeping the other parameters constant. As shown in Table 3, the use of Ru(pbbp)(pydic) is essential. Only 47.3% conversion of 1-phenylethanol was achieved in 10 h in the absence of the catalyst (Table 3, entry 1). Increasing the amount of catalyst from 0.05 to 0.2 mol%, the reaction time required to finish the reaction decreased from 5 h to 1.5 h (Table 3, entries 2–4). However, when the catalyst loading was increased from 0.1 to 0.2 mol%, only 0.5 h was saved to finish the reaction. Therefore, the optimal loading of Ru(pbbp)(pydic) was chosen as 0.1 mol%.

Fig. 5 SEM images of pbbp (**a**), fresh Ru(pbbp)(pydic) (**b**), Ru(pbbp)(pydic) after the first run (**c**) and Ru(pbbp)(pydic) after the third run (**d**)

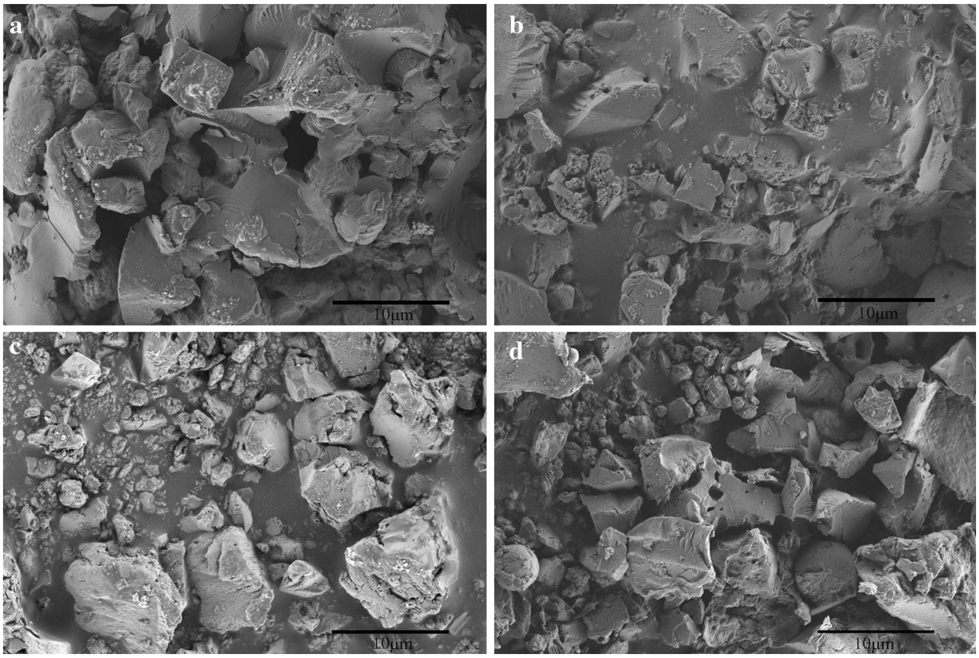
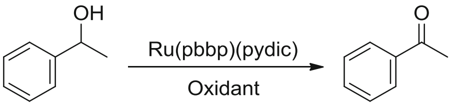


Table 1 Oxidation of 1-phenylethanol catalyzed by Ru(pbbp)(pydic) with different oxidants



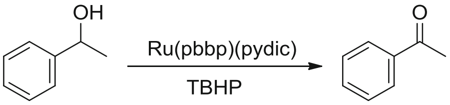
Entry	Oxidant[a]	Solvent	Time (h)	Conv. (%)[b]	Select. (%)[b]
1	O_2	–	5.0	–	–
2	30% H_2O_2	–	5.0	46.1	>99
3	70% TBHP	CH_3CN	5.0	74.0	>99
4	70% TBHP	MeOH	5.0	65.6	>99
5	70% TBHP	Toluene	5.0	59.2	>99
6	70% TBHP	AcOEt	5.0	52.0	>99
7	70% TBHP	–	4.0	>99	>99

Reaction condition 1-phenylethanol (2 mmol), catalyst (0.1 mol%), oxidant (6 mmol), solvent (2 ml), reaction temperature 40 °C

[a] O_2 1 atm

[b] Determined by GC

Table 2 Effect of reaction temperature on the oxidation of 1-phenylethanol

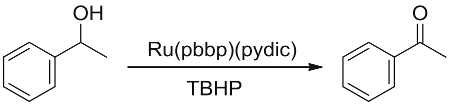


Entry	Temperature (°C)	Time (h)	Conv. (%)[a]	Select. (%)[a]
1	25	15.0	>99	>99
2	40	4.0	>99	>99
3	60	2.0	>99	>99
4	80	1.0	>99	>99

Reaction condition 1-phenylethanol (2 mmol), catalyst (0.1 mol%), oxidant (6 mmol)

[a] Determined by GC

Table 3 Effect of the amount of catalyst on the oxidation of 1-phenylethanol



Entry	Ru(pbbp)(pydic) (mol%)	Time (h)	Conv. (%)[a]	Select. (%)[a]
1	–	10.0	47.3	>99
2	0.05	5.0	>99	>99
3	0.1	2.0	>99	>99
4	0.2	1.5	>99	>99

Reaction condition 1-phenylethanol (2 mmol), oxidant (6 mmol), reaction temperature 60 °C

[a] Determined by GC

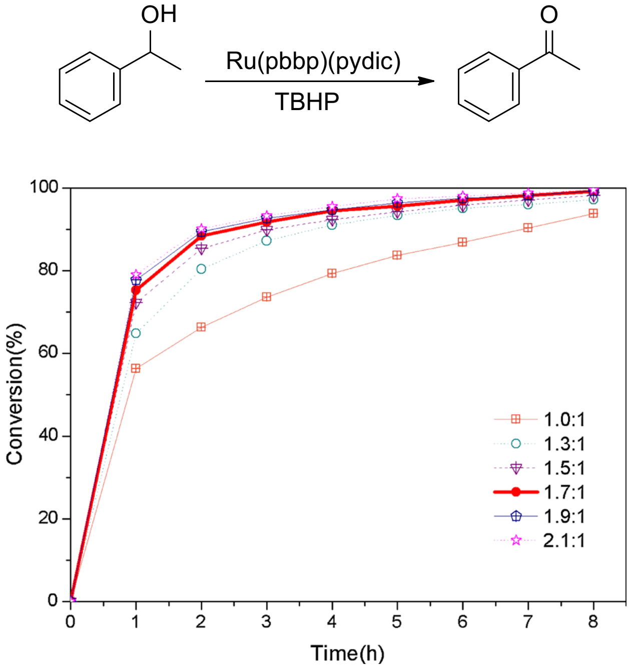


Fig. 6 Effect of the amount of TBHP on the oxidation of 1-phenylethanol

Generally, increasing the amount of TBHP can accelerate the reaction effectively. However, excessive TBHP will cause work-up complications and generate additional wastes. In order to avoid over-loading of TBHP, the oxidation reaction was tracked under the molar ratio of oxidant to substrate from 1.0:1 to 2.1:1, and the results are shown in Fig. 6. As shown in Fig. 6, the conversion of 1-phenylethanol increased with reaction time under all TBHP loadings. However, the reaction could not finish in 7.5 h if the molar ratio of TBHP to substrate was lower than 1.7:1. When the molar ratio of TBHP to substrate was equal to or higher than 1.7:1, the reaction could finish in 7.5 h. Therefore, the most suitable molar ratio of TBHP to 1-phenylethanol was 1.7:1. In this case 1-phenylethanol was almost quantitatively converted to acetophenone in 7.5 h.

Based on the experimental results, we concluded that the optimal conditions for the oxidation of 1-phenylethanol are substrate 2 mmol, catalyst 0.1 mol%, molar ratio of TBHP to substrate 1.7:1 and reaction temperature 60 °C. Under the optimal conditions, 1-phenylethanol was almost completely oxidized to acetophenone in 7.5 h in the absence of solvent.

Having obtained the optimal conditions, the Ru(pbbp)(pydic) was applied to the oxidation of various secondary and several primary alcohols to screen the versatility of the Ru(pbbp)(pydic)–TBHP. As shown in Table 4, most of the secondary benzylic alcohols, including the ones with both electron-donating and electron-withdrawing groups, were selectively converted to the corresponding ketones in high yields under the optimal reaction conditions (Table 4, entries 1–10, 13–15). However, the reaction rate changed with the substrate structures. Generally, the electron-donating substituents resulted in longer reaction times (Table 4, entries 2–10), which indicated that electronic properties of the substituents have some effects on the reaction. The substituent position on the benzene ring has obvious influence on the reactivity of the secondary benzylic alcohols. The substrate with an *o*-substituent reacted slowly compared to the one with an *m*- or *p*-substituent due to the steric hindrance of the *o*-substituent (Table 4, entries 2, 3, 5–7). For instance, only 38.5% conversion was obtained in the oxidation of 1-(2-chlorophenyl)ethanol in 12 h (Table 4, entry 7). Higher TBHP loading and longer reaction time were required to get high yields in the oxidation of 1-(2-chlorophenyl)ethanol and 1-(2-methylphenyl)ethanol (Table 4, entries 4, 8). The length of the aliphatic chain of the substrate has obvious effect on the reaction. Only 59.6% conversion was obtained in 14 h under the optimized conditions in the oxidation of 1-phenyl-1-propanol (Table 4, entry 11). Increasing TBHP loading and extending reaction time improved the reaction. When the molar ratio of TBHP to substrate was increased to 2.2:1, 1-phenyl-1-propanol was quantitatively converted to propiophenone in 16 h (Table 4, entry 12). Overall, the reaction of the secondary alcohols was controlled by the combined results of electronic and steric effects. The Ru(pbbp)(pydic) showed moderate activity in the oxidation of secondary aliphatic alcohols (Table 4, entries 16–21), which are poor substrates in the oxidation with other transition metal catalyst systems [14, 35]. Due to the big steric hindrance in the structure 2-isopropyl-5-methylcyclohexanol gave very low conversion (Table 4, entries 22, 23). The catalytic oxidation system was also used in the oxidation of several primary benzylic alcohols to screen whether it is feasible to get either the aldehyde or the carboxylic acid. The results indicated that it is difficult to control the selectivity, and the main products were the corresponding carboxylic acids in all the cases (Table 4, entries 24–28).

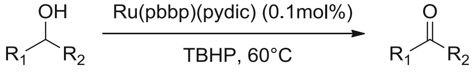
Recycling of catalyst

Finally, a recycling test was carried out to evaluate the stability as well as the reusability of Ru(pbbp)(pydic). For each cycle, the catalyst was separated from the reaction mixture by filtration, washed extensively with methanol and dried thoroughly. The recovered catalyst was subjected to the next run under the same experimental conditions. The results are summarized in Table 5. Comparing the results in the second run with those in the first run, the conversion of 1-phenylethanal decreased by about 6.1%. In the third run, the conversion of 1-phenylethanal to acetophenone was only 70.8% in 7.5 h. To elucidate the deactivation reasons, the ruthenium content of the filtrate after each run was analyzed using ICP, and the results are presented in Table 5. The ICP analysis confirmed the presence of ruthenium in the filtrate, which was the deactivation reason of the Ru(pbbp)(pydic) catalyst. In order to investigate whether the leakage of ruthenium into filtrate is caused by dissolving of the polymer ruthenium complex in the reaction mixture or breaking down from the polymer ligand, an additional catalytic experiment was carried out. To the filtrate of the first run was added 5 mmol of 1-phenylethanol, then 8.5 mmol of TBHP was dropped slowly, the 1-phenylethanol was almost quantitatively converted to acetophenone with extending reaction time. This result indicated that the deactivation of the polymer–ruthenium is mainly due to the dissolution of the ruthenium complex into the reaction mixture.

In view of the above results, the recycling procedure for the catalyst was changed to the following manner. After each catalytic run, the product acetophenone was distilled off in vacuum and the residue was used directly in the subsequent run. The results listed in Table 6 show that the conversion of 1-phenylethanol decreased slightly in the second run. The reusability of the Ru(pbbp)(pydic) catalyst was improved in this manner compared to recycling the catalyst by filtration. However, the catalyst still deactivated gradually with further recycling. In the fourth run, the conversion of 1-phenylethanal to acetophenone was 84.8% in 7.5 h. In this case the deactivation of the Ru(pbbp)(pydic) catalyst could be ascribed to the decomposition of the complex in the catalytic run.

A hot filtration test was carried out to confirm the heterogeneity of the reaction. In the experiment 0.1% mol of Ru(pbbp)(pydic) was suspended in the mixture of solvent and 1-phenylethanol or neat 1-phenylethanol under stirring for 30 min at 60 °C, and then the catalyst was removed by hot filtration. The filtrate was subjected to oxidation by TBHP. The reaction processes were monitored by GC, and the results are listed in Table 7. For comparison, the oxidation of 1-phenylethanol both in the absence and in the presence of Ru(pbbp)(pydic) was also performed, and the results are listed in Table 7, too. From the table, it can be seen that low conversion of 1-phenylethanol was obtained in the oxidation of the filtrates in 5 h, no matter whether the extracts are acetonitrile, toluene and 1-phenylethanol itself (Table 7, entries 1–3). Slightly low conversion of 1-phenylethanol was received in the absence

Table 4 Oxidation of various alcohols with TBHP catalyzed by Ru(pbbp)(pydic)



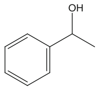
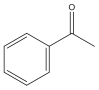
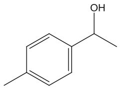
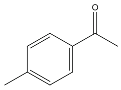
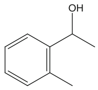
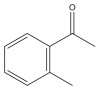
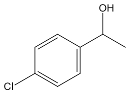
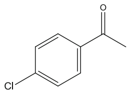
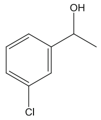
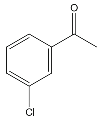
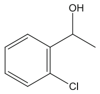
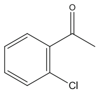
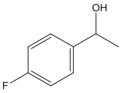
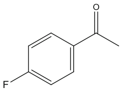
Entry	Substrate	Product	Time (h)	Conv. (%)[a]	Select. (%)[a]	Yield (%)[b]
1			7.5	>99	>99	95.0
2			11	>99	>99	94.1
3			15	62.8	>99	49.7
4[c]			20	>99	>99	88.2
5			8	>99	>99	95.2
6			18	>99	>99	93.3
7			12	38.5	>99	28.5
8[c]			24	>99	>99	90.2
9			7.5	>99	>99	90.1

Table 4 continued

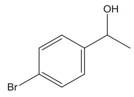
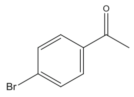
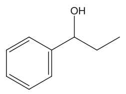
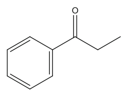
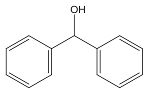
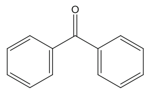
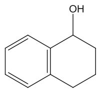
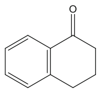
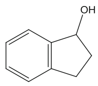
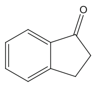
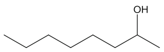
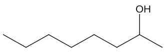
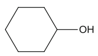
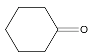
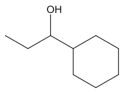
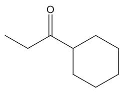
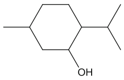
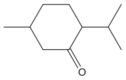
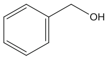
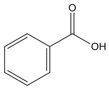
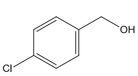
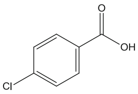
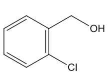
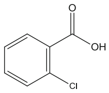
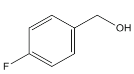
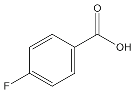
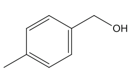
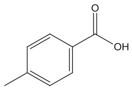
10			9	>99	>99	96.6
11			14	59.6	>99	48.9
12[d]			16	>99	>99	93.7
13			4	>99	>99	97.6
14			10	>99	>99	89.0
15			5	>99	>99	90.1
16			17.5	67.3	>99	55.6
17[c]			17	>99	>99	83.4
18			21	57.9	>99	41.0
19[e]			17	>99	>99	80.2
20			33	56.4	>99	42.0

Table 4 continued

21[c]			25	>99	>99	84.6
22			9	17.2	>99	
23[c]			17	39.2	>99	
24[d]			10	99.7	97.4	89.7
25[d]			16	97.8	66.6	51.9
26[c]			12	95.9	62.8	49.0
27[d]			16	98.0	75.6	61.3
28[d]			15	95.1	92.8	78.3

Reaction conditions alcohol (2 mmol), oxidant (3.4 mmol), catalyst (0.1 mol%), reaction temperature 60 °C

[a] Determined by GC

[b] Isolated yields, the product was purified by column chromatography over silica gel (eluent: *n*-hexane/ethyl acetate)

[c] Oxidant: 6 mmol

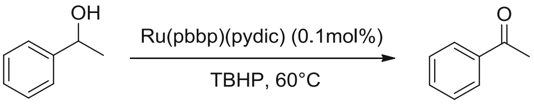
[d] Oxidant: 4.4 mmol

[e] Oxidant: 4 mmol

All products were determined by ^{1}H NMR

of catalyst compared to that in the oxidation of 1-phenylethanol filtrate (Table 7, entry 4). However, the conversion of 1-phenylethanol reached up to 95.6% in the presence of Ru(pbbp)(pydic) (Table 7, entry 5). The results indicated that the solubility of Ru(pbbp)(pydic) in the reaction mixture was very low during the reaction, and most of the reaction was catalyzed by the Ru(pbbp)(pydic) in solid state.

Table 5 Recycling of Ru(pbbp)(pydic) in the oxidation of 1-phenylethanol by filtration



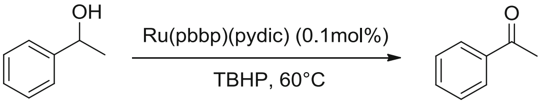
Entry	Run	Conv. (%)[a]	Select. (%)[a]	Ru (%)[b]
1	1	>99	>99	10.6
2	2	93.9	>99	11.5
3	3	70.8	>99	18.4

Reaction condition 1-phenylethanol (50 mmol), catalyst (0.05 mmol), oxidant (85 mmol), reaction temperature 60 °C, reaction time 7.5 h

[a] Determined by GC

[b] The percentage of ruthenium in filtrate with the catalyst loading in the first run

Table 6 Recycling of Ru(pbbp)(pydic) in the oxidation of 1-phenylethanol



Entry	Run	Conv. (%)[a]	Select. (%)[a]
1	1	>99	>99
2	2	97.4	>99
3	3	92.3	>99
4	4	84.8	>99
5	5	77.2	>99

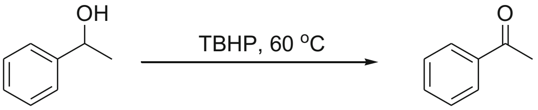
Reaction condition 1-phenylethanol (50 mmol), catalyst (0.05 mmol), oxidant (85 mmol), reaction temperature 60 °C, reaction time 7.5 h

[a] Determined by GC

Conclusions

The polymer pbbp in combination with pydic reacted with $RuCl_3$ to afford a polymer–ruthenium complex Ru(pbbp)(pydic) successfully. The percentage of complexation of 2,6-bis(benzimidazol-2-yl)pyridine unit in pbbp was about 83%. Ru(pbbp)(pydic) is an efficient catalyst for the oxidation of various secondary alcohols including aromatic and aliphatic ones to the corresponding ketones with TBHP as oxidant under solvent-free conditions and low catalyst loading. Due to the slight dissolution of Ru(pbbp)(pydic) in the reaction system, recycling of the catalyst by simple filtration was not satisfactory. Efforts are currently underway to synthesize the polymer with higher molecular weight to decrease its solubility in solvents, which will decrease the solubility of the polymer–ruthenium complex in solvents and improve its recyclability in catalysis.

Table 7 Oxidation of 1-phenylethanol in hot filtrates with TBHP



Entry	Filtrate	Conv. (%)[a]	Select. (%)[a]
1	1-Phenylethanol/CH_3CN	27.7	>99
2	1-Phenylethanol/Toluene	19.4	>99
3	1-Phenylethanol	25.4	>99
4[b]	_	22.8	>99
5[c]	_	95.6	>99

Reaction condition 1-phenylethanol (2 mmol), oxidant (3.4 mmol), solvent (2 ml), reaction temperature 60 °C, reaction time 5 h

[a] Determined by GC

[b] The oxidation of 1-phenylethanol with TBHP in the absence of catalyst

[c] The oxidation of 1-phenylethanol with TBHP in the presence of 0.1% mol of catalyst

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