NJC





Cite this: New J. Chem., 2019, 43, 19415

Received 24th August 2019, Accepted 17th November 2019

DOI: 10.1039/c9nj04393d

rsc.li/njc

Introduction

The selective oxidation of alcohols to the corresponding carbonyl compounds attracted increasing attention in recent years.¹⁻⁴ Acceptorless alcohol dehydrogenation (AAD) without any oxidizing reagents is a superior protocol from a green chemistry viewpoint.¹ Dehydrogenative oxidation of alcohols to carbonyl compounds catalyzed by homogeneous transition metals like ruthenium and^{5,6} iridium⁷⁻⁹ have been well reported. Other classical methods for the oxidation of alcohols have been well developed. Metal oxidizing reagents are used in stoichiometric amounts but known to be hazardous or toxic.¹⁰⁻¹² The need for environmentally benign and clean oxidation reactions becomes an important goal of chemical research.^{13–16} By comparing different oxidation methods in the presence of an oxidant, it is apparent that the oxidants employed for respective transformation define the quality and applicability of the method. Like molecular oxygen, hydrogen peroxide is an environmentally

Efficient and selective oxidation of alcohols to carbonyl compounds at room temperature by a ruthenium complex catalyst and hydrogen peroxide[†]

In this study, convenient and selective oxidation of alcohols using aqueous hydrogen peroxide to yield carbonyl compounds was studied. Using the ruthenium-(4-methylphenyl-2,6-bispydinyl) pyridinedicarboxylate complex [Ru(mpbp)(pydic)] as a catalyst, primary and secondary alcohols were oxidized to aldehydes and ketones at room temperature with a satisfactory yield and excellent selectivity. The influence of various reaction parameters, such as solvent, catalyst and oxidant amount on both the activity and selectivity was also evaluated. Kinetic studies showed that the oxidation of alcohol was first order in terms of the substrate and hydrogen peroxide, and was second order in terms of the catalyst. A plausible mechanism involving ruthenium-oxo species with electrophilic character was proposed based on the *in situ* UV-vis spectroscopy studies and Hammett plots.

> benign oxidant, which should theoretically generate only water as a by-product.^{17–20} In regard to this, various transition metal-based catalysts, including manganese salts,^{21–23} iron complexes,^{24–26} copper,^{27,28} gold nanoparticles,^{29–31} MnO₂³² and Ni-base catalysts^{33–35} have so far been intensively investigated for their oxidation activities of alcohols.

> During the past decades, ruthenium complexes containing nitrogen-based ligands like porphyrins and pyridines have intensively been studied for developing organic oxidation catalysts.^{36–40} Carbonyl ruthenium pentalfluorophenyl porphyrins present high oxidation activities towards the catalysis of secondary aromatic alcohols with tetrabutyl ammonium hydroxide as an oxidant.³⁸ In view of this, our group has so far reported an efficient oxidation process of alcohol catalyzed by ruthenium tetraphenyl-porphyrins in the presence of molecular oxygen.⁴¹

Substituted pyridines are particularly attractive ligands, and ruthenium(n) complexes containing pyridine ligands have received increasing attention in catalytic oxidation processes. Specifically, half sandwiched ruthenium(n) complexes containing 2.6-bis((phenylseleno)methyl)pyridine are effective catalysts for alcohol oxidation using *N*-methylmorpholine-*N*-oxide (NMO) as an oxidant.⁴² Nishiyama *et al.* reported an asymmetric epoxidation using the ruthenium complex 2,6-dicarboxylate (pydic).⁴³ Beller's research group developed efficient asymmetric epoxidation processes using greener oxidants, such as hydrogen peroxide and *tert*-butylhydroperoxide (TBHP).⁴⁴ In our previous work, we reported efficient oxidation of alcohol catalyzed by Ru(bbp)(pydic) under solvent-free conditions.⁴⁵ Recently, Zhao's group employed



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^a School of Chemical Engineering, Guangdong University of Petrochemical Technology, Maoming 515000, P. R. China

^b School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, P. R. China. E-mail: zhouxtai@mail.sysu.edu.cn

^c Fine Chemical Industry Research Institute, The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, P. R. China.

E-mail: jihb@mail.sysu.edu.cn

 $[\]dagger$ Electronic supplementary information (ESI) available: MS spectra, GC spectra, ESR spectra and kinetics studies. See DOI: 10.1039/c9nj04393d



Scheme 1 1: [Ru(mpbp)(pydic)], ruthenium-4-methylphenyl-2,6-bispydinylpyridinedicarboxylate; 2: [Ru(mpbmp)(pydic)], ruthenium-4-methylphenyl-2,6-bis(4-methyl)pydinyl-pyridinedicarboxylate.

the poly(pbbp)(pydic) ruthenium complex as a heterogeneous catalyst for the oxidation of alcohol using TBHP as an oxidant.⁴⁶

Previously, we introduced pyridinedicarboxylate as counterparts to synthesize new catalysts with dual closed meridional stereotypes around active metals. Here, we used (4-methylphenyl-2,6-bispydinyl)pyridine and pyridinedicarboxylate to successfully prepare the ruthenium complex Ru(mpbp)(pydic) (Scheme 1), which then was tested as a catalyst in oxidation reactions. The as-prepared ruthenium complex was found to be efficient for the selective oxidation of alcohols to the corresponding carbonyl compounds in the presence of hydrogen peroxide at room temperature. A plausible mechanism involving one electrophilic Ru-oxo species was proposed to explain the process.

Results and discussion

alcohol by the ruthenium complex and H₂O₂^a

OН

1.0

2.0

3.5

4.0

4

5

6

7

8

9

1

1

1

1

Catalytic performance

To explore the reactivity and selectivity of the as-prepared Ru(mpbp)-(pydic) catalyst, benzyl alcohol was used as a model substrate. In control experiments without the catalyst, no obvious conversion of alcohols was observed (entry 1, Table 1). A comparison between the tested catalysts revealed that ruthenium complex 1 exhibited higher catalytic activity than ruthenium complex 2 (entries 2 and 3, Table 1). These catalytic differences could be ascribed to the electric potential and stability of ruthenium metal atoms, yielding different electronic effects in the substituted group.

Next, ruthenium complex 1 was utilized as a catalyst to determine the optimal reaction conditions by varying the amount of H2O2 and solvents. The yield of benzaldehyde increased as the oxidant amount increased (entries 4-7, Table 1). The large excess amount of H2O2 could promote over-oxidation of benzaldehyde to benzoic acid, resulting in decreased selectivity towards benzaldehyde (entries 6 and 7, Table 1).

The effect of the solvent on the oxidation of benzyl alcohol was examined in the presence of the Ru(mpbp)(pydic) catalyst and aqueous hydrogen peroxide. After considerable optimization of the solvent, less-polar solvents like dichloromethane and cyclohexane resulted in a low yield of benzaldehyde (entries 8 and 9, Table 1). A moderate yield of benzaldehyde was obtained using ethyl acetate and ethanol (entries 10 and 11, Table 1). Interestingly, the catalyst resulted in excellent conversion to benzaldehyde with 97% yield in acetonitrile as the solvent (entry 2, Table 1).

Subsequently, the catalyst amount employed for selective oxidation of benzyl alcohol was examined and the data are shown in Fig. 1. It is noted that a low amount of catalysts led to less efficient catalysis under the same reaction conditions. The yield of benzaldehyde increased as the catalyst amount increased. However, no significant difference in efficiency was observed as the amount of catalyst was enhanced. However, excess catalyst showed declined selectivity toward benzaldehyde.

To further identify the scope of alcohol reactions using $Ru(mpbp)(pydic)-H_2O_2$ as the catalyst, the study was extended to include various primary alcohols and the results are summarized in Table 2. The catalytic system appeared efficient towards most primary alcohols, in which the alcohols were smoothly converted to the corresponding carbonyl compounds with high conversion rates and excellent selectivities (entries 1-7, Table 2). Compared to benzylic alcohol with electron-withdrawing groups at the para position o, electron-donating groups seemed more favorable for forming carbonyl compounds (entries 2-5, Table 2). This was inefficient for basic substrates like 4-pyridinemethanol (entry 6, Table 2), where 68% conversion was obtained after a prolonged reaction time of 90 min. The catalytic system



CH₃CN, room temperature Conv. (%) Yield (%) Entry Catalyst H₂O₂ (equiv.) Solvent Acetonitrile 1 None 3.0 2 3.0 Acetonitrile 98 97 1 3 2 3.0 Acetonitrile 87 85

Acetonitrile

Acetonitrile

Acetonitrile

Acetonitrile

1 or 2

Table 1 Optimization of the oxidation reaction conditions of benzyl

8	1	3.0	Dichloromethane	35	34
9	1	3.0	Cyclohexane	32	29
10	1	3.0	Ethyl acetate	68	65
11	1	3.0	Ethanol	63	59
^a Bei	nzyl al	cohol (1 mmol), solvent (2 mL), catal	yst (0.1	mol%), 25 °C

and 60 min.

Fig. 1 Effect of the catalyst amount on benzyl alcohol oxidation (A: 0.001 mol%, B: 0.01 mol%, C: 0.1 mol%, and D: 1.0 mol%). Conditions: benzyl alcohol (1 mmol), acetonitrile (2 mL), H₂O₂ (3.0 equiv.), 25 °C, and 60 min

°0

55

71

91

86

56

72

99

99

Table 2 Oxidation of various alcohols with H_2O_2 catalyzed by Ru(mpbp)(pydic)^a $% \left(\frac{1}{2}\right) = \frac{1}{2}\left(\frac{1}{2}\right) \left(\frac{1}{2}\right)$

Entry	Substrate	Product	Time/min	Conv./%	Yield ^b /%
1	ОН	0	60	98	92
2	ОН	0	60	99	93
3	МеО	MeO	60	99	96
4	O2N OH	0 ₂ N	90	82	80
5	СІОН	CI	60	85	80
6	ОН	N O	90	68	62
7	∽∽∽ОН	∽∽∽∕≈0	60	93	90
8	OH	° C	60	98	933
9	ОН	₽₽°	90	82	78
10	ОН	o	60	92	90
11	ОН		60	96	90
12	ОНОН	ОН	60	98	81 ^c
13	ОН	ОН	60	94	90 ^c
14^d	ОН	ОН	60	93	63(30) ^c

 a Substrate (1 mmol), catalyst (1 \times 10 $^{-3}$ mmol), acetonitrile (2 mL), H₂O₂ (3.0 equiv.), and 25 °C. b Isolated yield. c GC yield. d The number in parenthesis shows the yield of cinnamaldehyde.

also showed relevant efficacy towards the oxidation of saturated primary aliphatic alcohols, such as 1-hexanol (entry 7, Table 2).

Furthermore, the [Ru(mpbp)(pydic)] system was found to be selective and efficient towards the oxidation of secondary alcohols (entries 8–11, Table 2). Even sterically hindered alcohols, such as 2-adamantanol, could smoothly be converted into carbonyl compounds (entry 9, Table 2). On the other hand, secondary cyclic alcohols, including cyclohexanol, were efficiently oxidized with 91% yield (entry 10, Table 2). In one substrate combining both primary and secondary hydroxyls, the experiments showed that secondary hydroxyls were easier to oxidize (entry 12, Table 2). A similar phenomenon was also observed in the oxidation of hexane-1,2-diol (entry 13, Table 2). As to cinnamyl alcohol carrying both the C=C bond and the hydroxyl group, the C=C bond was preferentially activated to generate the corresponding epoxide as the main product with 63% yield (entry 14, Table 2).

Kinetics and mechanism

To explore the mechanism of the aqueous oxidation of alcohols using benzyl alcohol as the model substrate, reaction kinetics studies were conducted. The factors influencing the rate of benzyl alcohol oxidation, such as the effects of the substrate concentration, catalyst and hydrogen peroxide, were all examined. The initial rate of benzyl alcohol was measured as a function of the consumed concentration of benzyl alcohol.

The kinetic studies were carried out in aqueous medium under pseudo-first order conditions. The results were found to fit the following rate equation (eqn (1)):

$$Rate = k[Sub]^{a}[Cat]^{b}[H_2O_2]^{c}$$
(1)

where [Sub], [Cat] and $[H_2O_2]$ are the concentrations of benzyl alcohol, catalyst and hydrogen peroxide, respectively, and *a*, *b* and *c* are the orders of the reaction.

Assuming that the catalyst concentration was constant during the oxidation and hydrogen peroxide was present in large excess, eqn (1) can be converted to eqn (2):

$$Rate = k_{obs} [Sub]^a$$
(2)

where k_{obs} is the observed pseudo-first-order rate constant of benzyl alcohol. By taking the logarithms of both sides, eqn (2) yields eqn (3):

$$\ln(\text{Rate}) = \ln k_{\text{obs}} + a \ln[\text{Sub}]$$
(3)

Thus, the observed rate constant and the reaction order could be determined from the slope and intercept of the plot. The kinetic behaviors were measured at different initial concentrations of benzyl alcohol. The initial concentrations of benzyl alcohol in this catalytic oxidation system were: $0.01 \text{ mol } \text{L}^{-1}$, $0.02 \text{ mol } \text{L}^{-1}$, $0.03 \text{ mol } \text{L}^{-1}$, and $0.05 \text{ mol } \text{L}^{-1}$. The obtained data are summarized in Table 3, and the logarithmic plot between the reaction rate and the concentration of benzyl alcohol is presented in Fig. S1 (ESI[†]). All the kinetic experiments showed good fits with first-order kinetics, implying that the reactions were first order in terms of benzyl alcohol.

At constant [Sub] = 2.0×10^{-2} mol L⁻¹ and [Cat] = 2.0×10^{-5} mol L⁻¹, the kinetic studies were carried out at various initial concentrations of hydrogen peroxide to induce rate constants whose values depend on [H₂O₂]. The substrate concentrations as a function of time are presented in Fig. 2. The observed rate constants could be determined from the slope at different initial concentrations of hydrogen peroxide. The pseudo first-order rate constants k_{obs} (min⁻¹) increased with [H₂O₂]. This indicated that the reaction obeyed first order with respect to [H₂O₂]. This was confirmed by the linear plots of

 Table 3
 The observed rate constant and the reaction order at different initial concentrations of the substrate

$[Sub] \times 10^2/M$	а	$k_{ m obs} \left(\times 10^3 / { m min}^{-1} \right)$	R^2
1.0	1.04	6.67	0.998
2.0	0.98	6.81	0.999
3.0	1.08	6.61	0.998
5.0	1.05	6.73	0.998



Fig. 2 The [Sub] vs. reaction time at different concentrations of hydrogen peroxide, 298 K, [Sub] = 2.0×10^{-2} mol L⁻¹, and [Cat] = 2.0×10^{-5} mol L⁻¹.

 $k_{\rm obs} \,({\rm min}^{-1}) \, vs. \,[{\rm H}_2{\rm O}_2]$ which yielded straight lines passing through the origin (Fig. S2, ESI†).

Assuming steady state conditions at the beginning of the reaction, it can be seen that the concentrations of benzyl alcohol and hydrogen peroxide were constant. The reaction rates were measured at constant [Sub] $(2.0 \times 10^{-2} \text{ mol } \text{L}^{-1})$ and $[\text{H}_2\text{O}_2]$ ($6.0 \times 10^{-2} \text{ mol } \text{L}^{-1}$) but different [Cat] (1.0×10^{-5} - $5.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$). The kinetic data were then fitted by the logarithm of the observed pseudo-first-order rate constant against the logarithm of the catalyst concentration (Fig. 3). The logarithmic plot estimated the reaction order to be about 2.0, suggesting that the reaction rate was second order in terms of the catalyst.

Oxidation reactions were also carried out at various temperatures ranging from 293 to 313 K and the results are shown in Table S1 (ESI[†]). The k_{obs} values increased as the temperature increased. The plot of log $k_{obs} vs. 1/T$ was a straight line (Fig. S3, ESI[†]). The value of activation energy (E_a) was calculated from the Arrhenius plot and estimated from the slope to be 56.1 kJ mol⁻¹.

To gain a better understanding of the mechanisms of ruthenium complex-catalyzed alcohol oxidation reactions, the



effects of the *para*-substituents on the reactivity of benzyl alcohol against *para*-substituted benzyl alcohol were examined. A good linear correlation was obtained when the $k_{\rm rel}$ values were plotted against the Hammett parameters of the substituents (Fig. 4). The small but negative ρ value (-0.31) indicated that the active intermediate possesses electrophilic character, consistent with oxidation of benzyl alcohol derivatives by a synthetic metal–oxo complex.^{47–49}

The ruthenium catalyst was monitored by in situ UV-vis spectroscopy (AvaSpec-2048X14 with a fiber optic probe) during the reaction with H_2O_2 (3.0 equiv.) at room temperature. Fig. 5 shows an initial characteristic absorption peak of Ru(mpbp)(pydic) at 288 nm. Note that the spectrophotometer was programmed to record the UV-vis spectra every 10 min. As the reaction proceeded, the peak at 288 nm gradually decreased in intensity. This change was attributed to the generation of a high-valent ruthenium complex during oxidation. The recorded spectroscopic features supported the conclusion that the complex was converted into ruthenium-oxo species.50-52 As reported previously by Beller, the ruthenium oxo complex was the active catalyst species in the asymmetric epoxidation system.44 As to Ru(mpbp)(pydic) in the presence of H_2O_2 , the reaction mechanism could also involve the participation of Ru-oxo species generated from the reaction between Ru(mpbp)(pydic) and hydrogen peroxide during oxidation. The formation of carbonyl compounds was attributed to the reaction of alcohol with Ru-oxo species, followed by β-hydride elimination. Further mechanistic studies on the active species are under investigation.

In addition, oxidation of deuterated benzyl alcohol (PhCD₂OH) was carried out. As shown in Table S2 (ESI[†]), after stirring for 60 min, only 12% PhCD₂OH was converted. The corresponding product was deuterated benzaldehyde (Fig. S4, ESI[†]). This suggested that the hydrogen abstraction occurred from the benzyl position of benzyl alcohol.

Besides, competitive oxidation of mixed substrates (PhCH₂OH and PhCD₂OH) was conducted under the same reaction conditions (Table S2, ESI \dagger). Non-deuterated benzyl alcohol could be oxidized completely, while the conversion of deuterated benzyl alcohol was only 18%. This indicated that the hydrogen



Fig. 3 The fit of the logarithmic curve of the observed pseudo-first order rate constant (ln k_{obs}) against the logarithm of the catalyst concentration (ln[Cat]). Conditions: 298 K, [Sub] = 2.0×10^{-2} mol L⁻¹, and [H₂O₂] = 6.0×10^{-2} mol L⁻¹.

Fig. 4 Hammett plot of $\log k_{rel}$ against the Hammett parameter (σ) for oxidation of *para*-substituted benzyl alcohols by Ru(mpbp)(pydic) and H₂O₂. Conditions: substrate (1 mmol), catalyst (1 × 10⁻³ mmol), aceto-nitrile (2 mL), H₂O₂ (3.0 equiv.), and 25 °C.

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Fig. 5 In situ UV-vis spectra of the Ru(mpbp)(pydic) catalyst during oxidation of benzyl alcohol in the presence of hydrogen peroxide (interval 10 min), benzyl alcohol (3 mmol), catalyst (3 \times 10⁻³ mmol), MeCN (6 mL), H₂O₂ (3.0 equiv.), and 25 °C



Scheme 2 Plausible mechanism of Ru(mpbp)(pydic)-catalyzed oxidation of alcohol in the presence of hydrogen peroxide.

abstraction that occurs from the benzyl position is the ratedetermining step. Such observations are consistent with alcohol oxidation catalyzed by Fe^V-bTMAL,⁵³ Mo(v)-porphyrin complex⁵⁴ and Ru_xTiO₂ catalyst.⁵⁵

Based on the above discussion, a plausible mechanism was proposed for the oxidation of benzyl alcohol in the presence of the ruthenium complex and hydrogen peroxide, and it is shown in Scheme 2.

The reaction should be initiated by the smooth interaction between the Ru(II) complex (a) and H_2O_2 to generate Ru(II)-OOH (b). Ru-oxo (c) was then generated from heterolytic cleavage of the O–O bond of species (b). Due to the electrophilic character of Ru-oxo (c), the substrate binds to Ru-oxo species to generate transition species (*d*). Then, β -hydride elimination proceeds to give the corresponding carbonyl compound. Further studies of the detailed mechanisms such as oxygen isotope, KIE (kinetic isotope effect) are in progress.

Experimental section

Reagents and methods

Chemicals were of analytical grade and purchased from Aldrich without further purification unless indicated. Solvents were of Scheme 3 The synthesis step of ruthenium complex catalysts.

analytical purity and used as received. Mass spectra were obtained on a Shimadzu LCMS-2010A spectrometer. Elemental analyses were carried out with an Elementar vario EL elemental analyzer. ¹HNMR was recorded on a Bruker AVANCE 400 spectrometer (500 MHz). IR spectra were recorded on a Bruker 550 FT-IR spectrometer. UV spectra were recorded on a Shimadzu UV-2450 spectrophotometer. The in situ UV-vis spectra of the ruthenium complex were recorded on a AvaSpec-2048 spectrometer. which was equipped with a high-pressure, high-temperature probe and connected to a stainless-steel reactor.

Synthesis of catalysts

[Ru(mpbp)(pydic)]. The synthesis routine for the ruthenium complex catalyst is shown as the following steps (Scheme 3). First, ruthenium intermediate b was synthesized by the reaction of a (0.646 g, 2 mmol) and RuCl₃·3H₂O (0.552 g, 2 mmol) in EtOH (50 mL) at 80 °C. After stirring for 4 h and solvent removal, ruthenium intermediate b was obtained in 82% yield. Then, 2,6-pyridinedicarboxylic acid (16.7 mg), ruthenium intermediate b (53 mg) and potassium carbonate (13.8 mg) were added in EtOH (50 mL). The whole reaction mixture was heated at 80 °C for 4 h. It turns deep purple after stirring for 15 min at 80 °C. The dark violet precipitate was collected by solvent removal to give a product (53.4 mg) in 85.7% yield. Structure characterization data: calc. for C29H20N4O4Ru: C, 59.08; H, 3.42; N, 9.50. Found: C, 58.71; H, 3.56; N, 9.35; IR (KBr)/cm⁻¹: 3450, 3032, 1620, 1473, 1093, 820, 784. UV-vis, CH_2Cl_2 , λ_{max} nm(relative intensity): 249(0.14), 288(0.45), 518(0.15). ¹H NMR: (500 MHz, CDCl₃): δ 10.54 (s, 3H), 9.96 (m, 4H), 9.26 (s, 2H), 8.50-8.87 (m, 4H), 8.03-8.26 (m, 4H), 3.78 (m, 3H), EI-MS: m/z 588.

The same procedure was used for the synthesis of ruthenium complex 2, [Ru(mpbmp)(pydic)] (yield 70.4%). Structure characterization data: calc. for C₃₁H₂₄N₄O₄Ru: C, 60.29; H, 3.92; N, 9.07. Found: C, 60.51; H, 3.96; N, 9.15; IR (KBr)/cm⁻¹: 3446, 3034, 2875, 1621, 1478, 824, 796. UV-vis, CH_2Cl_2 , λ_{max} nm (relative intensity): 249(0.14), 388(0.46), 518(0.15). ¹H NMR: (500 MHz, CDCl₃): δ 10.03 (s, 3H), 9.66 (m, 4H), 9.37 (s, 2H), 8.03-8.26 (m, 6H), 3.92-3.96 (m, 9H). EI-MS: m/z 617.

Catalytic oxidation of alcohol

Catalytic oxidation of alcohol was carried out in a magnetically stirred glass reaction tube fitted with a reflux condenser.



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The typical procedure using benzyl alcohol as the model substrate was as follows: benzyl alcohol (1 mmol) and Ru(mpbp)(pydic) $(1 \times 10^{-3} \text{ mmol}, 0.1 \text{ mol}\%$ based substrate) were added into a reaction tube. The reactor containing this mixture was stirred in an oil bath at room temperature, and then 30% H2O2 (3.0 mmol) was slowly dropped in. The resulting system was stirred for 60 min. At the end of the reaction, the resulting products and the unreacted substrate were extracted by using dichloromethane three times. The extracted liquid mixture was analyzed by GC and GC-MS. GC analyses were performed on a Shimadzu GC-2010 plus chromatograph equipped with an Rtx-5 capillary column (30 m \times 0.25 mm \times 0.25 μ m). GC-MS analyses were recorded on a Shimadzu GCMS-QP2010 chromatograph equipped with an Rxi-5ms capillary column (30 m \times 0.25 mm \times 0.25 μ m). The organic phase was dried with MgSO4, and the product was purified by column chromatography (silica as a stationary phase and CHCl₃ as an eluent). The yield of benzaldehyde (>99.5 purity) was 92%. Other products were obtained following the same purification procedures.

Conclusions

Efficient alcohol oxidation was catalyzed by using Ru(mpbp)(pydic) in the presence of hydrogen peroxide as an oxidant. Both primary and secondary alcohols were oxidized to their corresponding carbonyl compounds in good yield. The influence of various reaction parameters, such as solvent, catalyst and oxidant amount on the activity and selectivity was evaluated. The *in situ* UV-vis spectroscopy studies indicated generation of Ru–oxo species during the oxidation process. A plausible mechanism for the catalytic oxidation of the alcohol process was proposed.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was supported by the National Key Research and Development Program of China (2016YFA0602900), the National Natural Science Foundation of China (No. 21425627, 21878344 and 21576302), the Guangdong Technology Research Center for Synthesis and Separation of Thermosensitive Chemicals (2015B090903061) and the Science and Technology Innovation Teams Project of Huizhou (20131226121851953).

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