

Catalytic oxidation of alcohols with polymer-supported ruthenium complex under mild conditions

Qiao-xiang Kang, Ju-jie Luo, Yan-bin Bai, Zhi-wang Yang, Zi-qiang Lei *

Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Aning East Road 805, Lanzhou 730070, China

Received 25 January 2005; accepted 21 October 2005
Available online 18 November 2005

Abstract

Polymer-supported ruthenium-containing complex PS–Phen–Ru was synthesized (where PS = chloromethyl polystyrene resin, Phen = 1,10-phenanthroline) and was characterized by FT-IR, ICP, and XPS. The supported complex was used to catalyze the oxidation of primary aliphatic alcohols as well as aromatic alcohols in the presence of iodossylbenzene. The oxidations were carried out in acetonitrile solution, affording the corresponding aldehydes or ketones in high substrate conversion and high selectivities under mild reaction conditions. The catalyst can be easily prepared and can be recycled.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Alcohol; Catalytic oxidation; Polymer-supported; Ruthenium complex; Iodossylbenzene

1. Introduction

The oxidation of alcohols to their corresponding aldehydes and ketones is one of the significant important transitions in organic chemistry, both for fundamental research and industrial manufacturing [1]. The world-wide annual production of carbonyl compounds are mostly produced from the oxidation of alcohols [2–4]. Aimed at avoiding the disadvantages of the traditional chromium reagents which cause serious environment pollution [5], many of the new methods focused on catalytic oxidation of alcohols have been invented. Among these methodologies, ruthenium-containing complexes play an important role in the transition due to their high catalytic activities [6,7]. Csornyik and co-workers employed the combined catalysts $\text{RuCl}_2(\text{OAc})(\text{PPh}_3)/\text{hydronquinone}/\text{Co}(\text{salen})(\text{PPh}_3)$ to oxidize the alcohols. With this catalyst, some allyl alcohols as well as aryl alcohols can be oxidized to the corresponding carbonyl products [8]. Wynne and co-workers [9] successfully

used another catalyst $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{MeOH})_3]^+\text{OAc}^-$ to oxidize some aliphatic alcohols to obtain the corresponding aldehydes. But all of these catalytic oxidation processes bear the shortcoming of difficulties in the preparation of the catalysts and in the separation of the catalysts from the reaction mixtures. On the other hand, all of these reported catalysts could not be recycled. We herein report the preparation and the catalytic property of a recyclable ruthenium-containing complex PS–Phen–Ru based on the chloromethyl polystyrene resin and 5-amino-1,10-phenanthroline. With the complex, many of alcohols, e.g., aryl alcohols as well as aliphatic alcohols, can all successfully oxidized to the corresponding aldehydes or ketones with high conversion and selectivity under mild conditions. Meanwhile, the catalyst can be recycled in the same reaction condition.

2. Experimental

2.1. Reagents

Chloromethyl polystyrene resin (PS– CH_2Cl), chlorine loading: 4.5 mmol/g, crosslink degree: 6%, aperture:

* Corresponding author. Tel./fax: +86931 7970359.
E-mail address: leizq@nwnu.edu.cn (Z.-q. Lei).

40–60 mesh, obtained from Tianjin Naikai Hecheng Science and Technology Co. Ltd. Iodosylbenzene (PhIO), purchased from ABCR GmbH & Co., 1,10-phenanthroline (Phen), purchased from Tianjin Tianxin Fine Chemical Plant. Other reagents and solvents were all obtained from commercial source and used as received without further purification. All of the reagents are analytical reagents.

2.2. Synthesis

2.2.1. Preparation of 5-amino-1,10-phenanthroline

5-amino-1,10-phenanthroline was prepared from 1,10-phenanthroline according to the literature procedure [10]. Generally, 1,10-phenanthroline was nitrated with concentrated nitric acid to afford 5-nitro-1,10-phenanthroline, and the product was then deoxidized by $\text{SnCl}_2/\text{HCl}(\text{conc.})$. The product was extracted with chloroform. After the remove of the solvent, the product then dried in vacuum, b.p 197–198 °C.

2.2.2. Synthesis of chloromethyl polystyrene supported 5-amino-1,10-phenanthroline

1.2 mg of chloromethyl polystyrene resin was swelled in 20 mL of 1,4-dioxane for 36 h. 0.55 g (2.54 mmol) of 5-amino-1,10-phenanthroline was added, the mixture was stirred for 1 h at 60 °C, 0.38 mL (1.42 mmol) of triethyl amine was then added to the solution, stirred for 24 h. 0.30 mL (1.02 mmol) of triethyl amine was added and stirred for 32 h, the solid was filtered, washed with distilled water and 1,4-dioxane, dried under vacuum at 45 °C overnight, the supported ligand PS–Phen was prepared.

2.2.3. Synthesis of chloromethyl polystyrene supported ruthenium complex

0.80 g of PS–Phen and 0.88 g of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ were added to 10 mL of THF, the mixture was stirred for 12 hours at room temperature. The product was filtered, washed with THF for several times, and then dried under vacuum at room temperature, the brown-colored product PS–Phen–Ru was obtained.

3. Results and discussion

3.1. Characterization of the complex

FT-IR spectra were taken on a Nicolet NEXUS 670 FT-IR chromatometer. It was showed that the N–Ru absorption signal in the complex was at 409 cm^{-1} . The content of ruthenium in the complex was 0.29% determined by an ARL-3520 ICP instrument. XPS analysis was carried out on PHI-550/ESCA/SAM multiple instrument. The results showed that the bind energy of the two kind nitrogen atoms in PS–Phen–Ru were increased 0.35 and 0.38 eV compared to those of the nitrogen in PS–Phen, respectively. Meanwhile, the bind energy of the ruthenium in the complex decreased 1.01 eV. All of these determination results confirmed that the complex was formed.

3.2. Catalytic properties for the oxidation of alcohols of the complex

3.2.1. Optimization of the oxidation conditions

The optimum conditions for the oxidation were concluded with benzyl alcohol as model substrate and iodosylbenzene as oxidant in the presence of the PS–Phen–Ru complexes in a 10-mL flask, equipped with a magnetic stirring bar.

3.2.1.1. The temperature. The oxidation was carried out at different temperatures, e.g., at 25, 40 and 60 °C, to find out the optimum temperature in order to achieve high product selectivity as well as high substrate conversion. All oxidation results at different temperatures were shown in the table (Table 1).

We can find from Table 1 that all the oxidations at different temperature give benzaldehyde as the only product and the conversion of benzyl alcohol reaches to 100% at 60 °C. It suggested that the optimum temperature of the oxidation is 60 °C.

3.2.1.2. The reaction time. The reaction was real-time monitored at about 0.5 h interval during the oxidation (benzyl alcohol 0.1 mmol, cat. 4 mg, PhIO 2.5 equiv., CH_3CN 2 mL, 60 °C). We can find that the conversion of benzyl alcohol was 76% within 1 h, and the substrate was fully oxidized to benzaldehyde within 2 h. On the other hand, the oxidation at different time bears the selectivity of 100% of benzaldehyde. This suggests that the optimum reaction time is 2 h at 60 °C.

3.2.1.3. The amount of the catalyst. As the ruthenium was supported by chloromethyl polystyrene, we investigated the amount of the catalyst just as 1, 2, 3 and 4 mg, respectively. In the same condition, each of the reaction gives different substrate conversion as was shown in Table 2.

Table 1
Catalytic oxidation of benzyl alcohol at different temperatures by PS–Phen–Ru

Entry	Temperature (°C)	Conversion (%)	Selectivity (%)
1	25	20	100
2	40	34	100
3	60	100	100

Condition: benzyl alcohol 0.1 mmol, cat. 4 mg, PhIO 2.5 equiv., CH_3CN 2 mL, 2 h.

Table 2
Catalytic oxidation of benzyl alcohol with different amount of PS–Phen–Ru

Entry	Catalyst (mg)	Conversion (%)	Selectivity (%)
1	1	46	100
2	3	95	100
3	4	100	100
4	5	100	100

Condition: benzyl alcohol 0.1 mmol, PhIO 2.5 equiv., CH_3CN 2 mL, 60 °C, 2 h.

We can find that the reaction using 4 mg of catalyst gives 100% conversion as well as 100% selectivity within 6 h. The same data were obtained by using 5 mg of catalyst, it means that the optimum amount of catalyst consumption is 4 mg in this oxidation system.

3.2.1.4. The amount of the iodosylbenzene. According to the literatures, when alcohol was oxidized by iodosylbenzene, the suitable amount of oxidant used ranged from 1.4 to 2.5 equiv. As for our novel catalytic system, we also investigated the amount of iodosylbenzene consumption in the oxidation. We changed the amount of oxidant from 0.5 to 2.5 equiv., the corresponding results were listed in the table (Table 3).

It showed in Table 3 that the utilization of 2.5 equiv. of iodosylbenzene afforded 100% benzyl alcohol conversion and 100% selectivity in the same condition. This suggested the suitable amount of oxidant in the oxidation was 2.5 equiv.

3.2.1.5. The solvent. The oxidation can be occurred in several solvents, such as dichloromethane (DCM), 1,2-dichloroethane (DCE), tetrahydrofuran (THF), toluene and acetonitrile. Among these solvents, acetonitrile serves as the most significant one under same reaction conditions. The conclusion can be verified with the results shown in the table (Table 4).

We can find from Table 4 that DCM and DCE can also give promising results, but we cannot carry on the oxidation at 60 °C. Meanwhile, CH₃CN gives the highest conversion under identical reaction condition.

From all of the investigation of the oxidation conditions, it can be concluded that the optimum condition for the oxidation is: catalyst 4 mg, iodosylbenzene 2.5 equiv., temperature 60 °C, solvent CH₃CN 2 mL.

3.2.2. Catalytic oxidation property for other alcohols

Many of other alcohols, including benzyl alcohol and its derivatives, benzhydrol and its derivatives, long-chained aliphatic alcohols as well as some general aliphatic alcohols, were well oxidized to the corresponding aldehydes or ketones with the PS–Phen–Ru complex under the optimum reaction conditions mentioned above. All of the oxidations bear the selectivities of 100% to the carbonyl

Table 3
Catalytic oxidation of benzyl alcohol by PS–Ru–Phen with different amount of PhIO

Entry	PhIO (g)	Conversion (%)	Selectivity (%)
1	0.011 (0.5 equiv.)	57	100
2	0.022 (1.0 equiv.)	75	100
3	0.033 (1.5 equiv.)	79	100
4	0.044 (2.0 equiv.)	86	100
5	0.055 (2.5 equiv.)	100	100

Condition: benzyl alcohol 0.1 mmol, cat. 4 mg, CH₃CN 2 mL, 60 °C, 2 h.

Table 4
Catalytic oxidation of benzyl alcohol with PS–Phen–Ru in different solvents

Entry	Solvent	Conversion (%)	Selectivity (%)
1	DCM	64	100
2	THF	37	100
3	Toluene	25	100
4	DCE	72	100
5	CH ₃ CN	100	100

Condition: benzyl alcohol 0.1 mmol, cat. 4 mg, PhIO 2.5 equiv., solvent 2 mL, 60 °C, 2 h.

products. Because of the different molecular structures of the alcohols, which, however, result in the different space hindrance between the substrates and the catalyst, the reaction time for each of the oxidation are not the same as that for the oxidation of benzyl alcohol. The results of the oxidations were concluded in the table (Table 5), and the corresponding reaction time needed to obtain the listed results was also listed in the table.

It shows in the Table 5 that: (i) the catalyst show promising catalytic activity for the oxidation of benzyl alcohol and its derivatives, benzhydrol and its derivatives, long-chained primary alcohols as well as some ordinary aliphatic alcohols with the oxidant of iodosylbenzene under mild reaction conditions. With the catalysis of the complex, all of the selected alcohols can be oxidized to the corresponding aldehydes or ketones with the selectivity of 100%. There is no by-product observed in these oxidations. (ii) Because of the different group of these alcohols, the reaction time of each oxidation reaction is not the same. We monitored each of the reaction, and decided the promising time for them. (iii) We can find that the catalytic activity of PS–Phen–Ru complex to each group of alcohols, e.g, benzyl alcohol and its derivatives, benzhydrol and its derivatives, long-chained primary alcohols and ordinary aliphatic alcohols, is differed due to different structures of these alcohols. The activity to benzyl alcohol and its derivatives is the best, whereas the activity to benzhydrol and its derivatives is not very good. This may come from the strong stereohindrance of the two benzene rings near the hydroxyl group in benzhydrol molecule, which hindered the electrophilic attack of the Ru atom of the catalyst to the oxygen atom of the substrate. (iv) This complex can catalyze the oxidation of aliphatic alcohols, which differed itself from other system. As we know, most of these substrates can not be easily oxidized unless a rigorous reaction condition was provided. It means that the catalytic system is a novel and more active one for the oxidation of alcohols.

3.3. The recycling property of PS–Phen–Ru

The supported catalysis is mostly aimed at the recycling of the catalyst. As for those rear metal-containing catalysts, this is something more significant than other considerations. Merrifield resin (chloromethyl polystyrene resin) is

Table 5
Catalytic oxidation of alcohols by PS–Phen–Ru(III) with PhIO as oxidant

Entry	Substrate	Product	Conversion (%)	Selectivity (%)	Time (h)
1			100	100	2
2			100	100	2
3			100	100	0.5
4			100	100	1
5			100	100	1
6			100	100	2
7			96	100	8
8			54	100	8
9			90	100	8
10			79	100	8
11			100	100	2
12			100	100	6
13			79	100	8
14			13	100	8

Condition: alcohol 0.1 mmol, PhIO 2.5 equiv., cat. 4 mg, CH₃CN 2 mL, 60 °C.

one of the most useful supporters. We find that our supported ruthenium complex can also be recycled in this oxidation system. The recycling results for the oxidation of benzyl alcohol are shown in the table (Table 6).

The results show that with the recycling, the activity of the catalyst decreased after the catalyst recycled for 3 times in the same reaction conditions. But when we increase the amount of catalyst used to 6 mg, the catalyst can be

Table 6
The recycling properties of supported PS–Phen–Ru catalyst

Times	Conversion (%)	Selectivity (%)
1	100	100
2	100	100
3	100	100
4	71	100
5	55	100

Condition: benzyl alcohol: 0.1 mmol, PhIO 2.5 equiv., cat. 4 mg, CH₃CN: 2 mL, 60 °C, 2 h.

recycled for at least 7 times without the obvious decrease of the catalytic activity in the same reaction conditions. In all the recycling, the selectivity to benzaldehyde is maintained 100%.

4. Conclusions

The chloromethyl polystyrene supported 5-amino-1,10-phenanthroline–ruthenium complex PS–Phen–Ru shows significant catalytic activity for the oxidation of alcohols, such as benzyl alcohol and its derivatives, benzhydrol and its derivatives, long-chained aliphatic alcohols, in the presence of iodobenzene under mild conditions. The oxidations all bear the selectivity of 100% to the correspond-

ing aldehydes or ketones. The catalyst can be recycled in the oxidations.

Acknowledgements

We thank National Natural Science Foundation of China for financial support (Grant Nos. 20174031 and 20474052).

References

- [1] R.C. Larock, *Comprehensive Organic Transformations*, VCH, New York, 1999.
- [2] S.V. Ley, J. Norman, W.P. Griffith, S.P. Marsden, *Synthesis* (1994) 639.
- [3] R.A. Sheldon, I.W.C.E. Arend, A. Dijkstra, *Catal. Today* 57 (2000) 157.
- [4] J. Muzart, *Tetrahedron* 59 (2003) 5789.
- [5] J. Muzart, *Chem. Rev.* 92 (1992) 113.
- [6] K. Ebitani, H.B. Ji, M. Tomoo, K. Kaneda, *J. Mol. Catal. A: Chem.* 212 (2004) 161.
- [7] A. Wolfson, S. Wuyts, D.E. de Vos, et al., *Tetrahedron Lett.* 43 (2002) 8107.
- [8] G. Csornyik, A.H. Ell, L. Fadini, et al., *J. Org. Chem.* 67 (2002) 1657.
- [9] J.H. Wynne, C.T. Lloyd, D.R. Witsil, et al., *OPPI BRIEFS* 32 (2000) 588.
- [10] (a) G.F. Smith, F.W. Lagle, *J. Org. Chem.* 12 (1947) 781;
(b) R.D. Gillard, E. Hill, *J. Chem. Soc., Dalton Trans.* (1974) 1217.