

Supported ionic-liquid layer on polystyrene–TEMPO resin: a highly efficient catalyst for selective oxidation of activated alcohols with molecular oxygen

Lin Liu · Dong Liu · Zhiwei Xia · Jiulin Gao · Tianlin Zhang · Juanjuan Ma · Dongen Zhang · Zhiwei Tong

Received: 16 November 2011 / Accepted: 24 April 2012 / Published online: 17 May 2012
© Springer-Verlag 2012

Abstract We report a facile, efficient procedure for selective oxidation of activated alcohols by use of a novel supported ionic-liquid catalyst produced by coating polystyrene–TEMPO resin with the ionic liquid [bmim]PF₆ and CuCl₂. The oxidation affords aldehydes or ketones in excellent yield and with high selectivity. It is worthy of note that the supported ionic-liquid layer substantially enhances catalytic activity, and the catalyst can easily be recycled.

Keywords Alcohol · Oxidation · Supported ionic liquid · TEMPO · Heterogeneous catalysis

Introduction

The transformation of alcohols into aldehydes and ketones is of great importance in organic chemistry, both in laboratory-scale experiments and in manufacturing processes [1]. Numerous oxidizing reagents (for example, CrO₃, KMnO₄, MnO₂, etc.) in stoichiometric amounts have been

traditionally used to accomplish this transformation, but with many drawbacks, for example use of expensive reagents, volatile organic solvents, and discharge of environmentally pernicious wastes. Environmentally and economically, catalytic oxidation processes are thus valuable, and those using molecular oxygen as primary oxidant are particularly attractive. Many highly efficient systems have been developed for catalytic aerobic oxidation of alcohols by use of transition metals alone (for example palladium [2–4], gold [5–7], ruthenium [8, 9], copper [10, 11], vanadium [12, 13]) or in combination with the nitroxyl radical 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO). Of particular interest are catalytic systems consisting of an inexpensive transition metal compound and TEMPO for mild and selective aerobic oxidation of alcohols. However, separation of the products from the TEMPO can require lengthy workup of these systems, especially for reactions on a large industrial scale.

In this context, use of a supported TEMPO catalyst seemed desirable, because it enables both catalyst recycling and simplified workup of the reaction mixture. TEMPO has been immobilized on inorganic and organic supports, for example SiO₂ [14, 15], molecular sieve [16], polymers [17–19], affording solid catalysts which are readily separated from the reaction mixtures. Nevertheless, these solid catalysts often have disadvantages of their own, and when oxygen, especially, is used as the terminal oxidant, supported TEMPO has less catalytic activity than under comparable homogeneous conditions [20, 21].

Ionic liquids (ILs) are, in contrast, eco-friendly reaction media or catalysts which have attracted increasing attention because of their particular properties—undetectable vapor pressure, high thermal stability, excellent solubility, and ease of recovery and reuse. However, ionic liquids are still expensive, despite being commercially available.

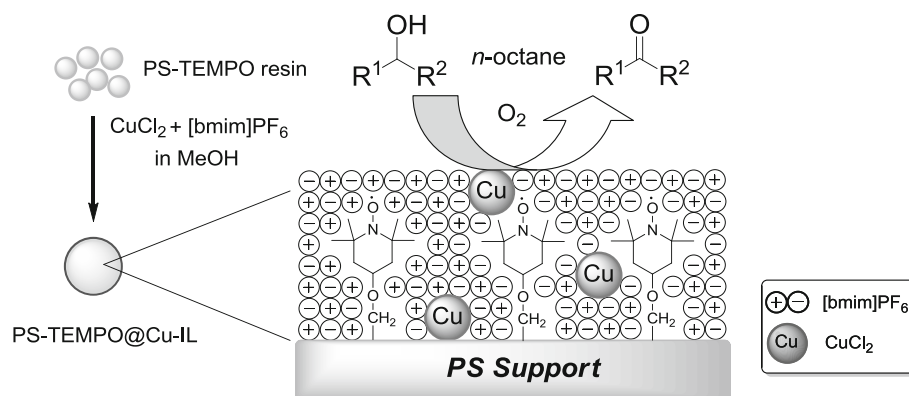
L. Liu · T. Zhang · J. Ma · D. Zhang
Jiangsu Marine Resource Development Research Institute,
Lianyungang 222005, China

L. Liu (✉) · D. Liu · Z. Xia · J. Gao · T. Zhang · J. Ma ·
D. Zhang · Z. Tong (✉)
Department of Chemical Engineering, Huaihai Institute
of Technology, Lianyungang 222005, China
e-mail: Spliulin@gmail.com

Z. Tong
e-mail: Zhiweitong575@hotmail.com

Z. Tong
SORST, Japan Science and Technology Agency (JST),
Kawaguchi-shi, Saitama, Japan

Fig. 1 Supported ionic-liquid catalytic system used for selective oxidation of alcohols



Furthermore, the high viscosity of ILs may result in mass transfer limitations if the chemical reaction is fast, causing the reaction to proceed in the diffusion layer of the catalyst rather than in the bulk solvent.

Recently, by analogy with well-established supported aqueous-phase catalysis [22], ILs have been introduced to the immobilization of homogeneous catalysts. The “solid catalyst with ILs (SCILs)” technique, in which the ionic liquid phase is immobilized as a film on a conventional supported catalyst, is a new method for circumventing the limitations described above [23, 24]. With SCILs, the activity and selectivity of the original solid catalyst may be changed substantially by coating its internal surfaces with the IL. Thus, processes have been designed for immobilization of ILs on solid catalysts [25–30].

Our recent work has focused on oxidation of organic compounds with molecular oxygen as the oxidant [31–34]. We have previously reported an efficient and recyclable catalyst system comprising CuCl_2 and TEMPO task-specific ionic liquid (TEMPO-IL), supported by the sol-gel technique [10] or by physical adsorption [35], for aerobic oxidation of alcohols. Herein, as part of our studies on the oxidation of organic compounds, we report a facile and efficient procedure for aerobic oxidation of alcohols to the corresponding carbonyl compounds by use of an effective and reusable catalyst prepared by coating the surface of ready-made polystyrene-TEMPO resin with the ionic liquid $[\text{bmim}]\text{PF}_6$ containing a copper salt (Fig. 1).

Results and discussion

Initial research was conducted with 4-methoxybenzyl alcohol as substrate to investigate the effects on the selective oxidation of the IL layer supported on the polystyrene-TEMPO (PS-TEMPO) resin; the results are summarized in Table 1. First, the catalytic activity of original PS-TEMPO resin was evaluated in different solvents. Among the solvents tested, catalytic activity of PS-TEMPO/ CuCl_2 was much greater in *n*-octane than in other solvents, with 58 % conversion and

Table 1 Effects of IL layer supported on PS-TEMPO resin on oxidation of 4-methoxybenzyl alcohol

Entry	Catalyst	Solvent	Conv. ^a /%	Select. ^a /%
1	PS-TEMPO/ CuCl_2	<i>n</i> -Octane	58	99
2	PS-TEMPO/ CuCl_2	Toluene	41	96
3	PS-TEMPO/ CuCl_2	$[\text{bmim}]\text{PF}_6$	24	58
4	PS-TEMPO/ CuCl_2	$[\text{bmim}]\text{BF}_4$	18	52
5	PS-TEMPO/ CuCl_2	DMF	5	–
6	PS-TEMPO@Cu-IL	<i>n</i> -Octane	85	>99
7 ^b	PS-TEMPO@Cu-IL	<i>n</i> -Octane	56	>99
8 ^c	PS-TEMPO@Cu-IL	<i>n</i> -Octane	59	>99
9	PS-TEMPO@Cu-IL	Toluene	55	>99
10	PS-TEMPO@Cu-IL	DMF	4	–
11	PS-TEMPO@Cu-IL	$[\text{bmim}]\text{PF}_6$	26	62

Reaction conditions: 1 mmol 4-methoxybenzyl alcohol, 100 mg PS-TEMPO@Cu-IL or 54 mg PS-TEMPO with 14 mg $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and 5 cm³ solvent under O_2 at 65 °C for 3 h

^a Conversion and selectivity (by GC)

^b 50 mg catalyst was used

^c Reaction temperature was 35 °C

99 % selectivity for benzaldehyde (entry 1). For the solvents toluene, $[\text{bmim}]\text{PF}_6$, and $[\text{bmim}]\text{BF}_4$, the rate of oxidation and the selectivity were substantially lower (entries 2–4). In DMF, the reaction barely proceeded (entry 5).

The activity and selectivity of the PS-TEMPO resin were increased substantially by the coating its surface with the IL. When *n*-octane was used as solvent, 85 % conversion was achieved with over 99 % selectivity, and similar results were observed in toluene. Immobilizing an IL layer on the solid support can have a marked effect on the catalytic activity of this system, improving the “chemical” properties of the catalyst (i.e. the cocatalytic effect), and providing higher effective concentrations of substrates or intermediates on the surface of the solid catalyst because of the ionic properties of the IL phase (i.e. a physical solvent effect) [23, 26]. In DMF or $[\text{bmim}]\text{PF}_6$ conversion and selectivity were still very low (entries 10, 11). Consequently, for this catalytic system, it is critical to

Table 2 Oxidation of alcohols with molecular oxygen catalyzed by PS-TEMPO@Cu-IL

Entry	Substrate	Product	Time/h	Conv./Select. ^a /%	Yield ^b /%
1	Benzyl alcohol	Benzaldehyde	6.5	97/>99	90
2	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	6.5	98/>99	94
3	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	7.5	96/>99	94
4	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	5	98/>99	93
5	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	5.5	98/>99	92
6	2-Methylbenzyl alcohol	2-Methylbenzaldehyde	6.5	99/>99	93
7	Cinnamyl alcohol	Cinnamaldehyde	12	97/97	91
8	Furfuryl alcohol	Furaldehyde	10	96/95	88
9	Cyclohexanol	Cyclohexanone	12	28/>99	–
10	1-Octanol	Octanal	12	10/>99	–

Reaction conditions: 1 mmol alcohol, 100 mg PS-TEMPO@Cu-IL, and 5 cm³ *n*-octane under O₂ at 65 °C

^a Conversion and selectivity (by GC)

^b Isolated yield

choose an appropriate solvent to form a biphasic system with ILs, otherwise the IL film would be washed off the catalyst, and the catalytic system would be deactivated.

After determining the optimum reaction conditions, we studied oxidation of a variety of alcohols catalyzed by PS-TEMPO@Cu-IL in *n*-octane; the results are listed in Table 2. All benzylic alcohols can be converted into the corresponding aldehydes with high conversion (entries 1–6). Similar reactivity was observed in the oxidation of substrates with electron-withdrawing or donating groups in the aromatic ring. The rates of these benzylic alcohol oxidations were not significantly affected by the electronic properties of the substituents on the benzene ring. Moreover, allylic and heterocyclic primary alcohols could be smoothly oxidized to the corresponding aldehydes, with high conversion, by use of this catalyst system (entries 7, 8). The catalytic system had high selectivity, and only traces of carboxylic acid (below 1 %), which was easily removed by washing the organic phase with sodium bicarbonate solution, were observed. The double bond of the allylic alcohol was unaffected. Despite the good results obtained for benzylic, allylic, and heterocyclic alcohols, conversion of aliphatic alcohols under the same conditions was quite low (entries 9, 10).

The reusability of the catalyst was investigated by using 4-methoxybenzyl alcohol as model substrate. The catalyst was easily recovered by filtration and washing with *n*-octane after the reaction. After being dried, it was subjected to another reaction with identical substrates. The procedure was repeated, and the results indicated that the catalyst could be cycled four times, with gradual loss of catalytic activity, with selectivity for aldehyde formation always remaining very high (Fig. 2). The structure of the catalyst recovered after five runs had not obviously changed, as was apparent from comparison of its FT-IR spectrum with that of the fresh catalyst. This result indicated that the TEMPO groups remained tightly bonded to the PS resin after five runs. In the supernatant fraction, Cu was not detected by ICP analysis. We suggested that the decrease in activity

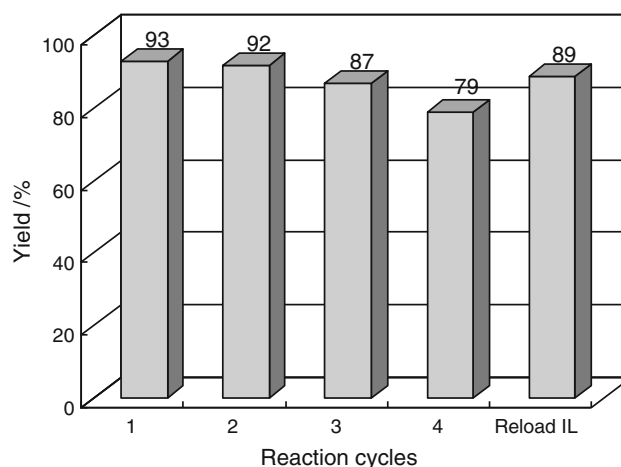


Fig. 2 Recycling of the catalyst used for selective oxidation of 4-methoxybenzyl alcohol

may be because of loss of [bmim]PF₆ adsorbed on the PS-TEMPO. To validate this postulate, the ionic-liquid layer was reloaded, and it was found that catalytic activity increased to a level close to that of the fresh catalyst.

In conclusion, we have developed a facile, efficient procedure for selective oxidation of activated alcohols by use of a novel ionic-liquid ([bmim]PF₆) catalyst containing CuCl₂ supported on PS-TEMPO resin. The supported ionic-liquid layer makes an important contribution to the high catalytic activity. Notable advantages of this method are high catalytic activity and selectivity, simple work-up, reusable catalyst, and mild reaction conditions.

Experimental

All chemicals were obtained from commercial sources; they were >99 % pure and used without prior purification. Gas chromatographic (GC) analysis was performed on a Shimadzu 17A equipped with a 30 m × 0.32 mm × 0.5 μm DB-5 capillary column and a flame ionization detector. Elemental analysis was performed by ICP–AES (Thermo icap 6300) and

use of a CHNS/O analyzer (PerkinElmer 2400 Series II). Infrared spectra were recorded as KBr disks on a Tensor 27 FT-IR spectrometer.

Catalyst preparation

Polystyrene-TEMPO resin was prepared in accordance with a literature method [19]; loading of the TEMPO was determined to be 0.90 mmol g⁻¹ by elemental analysis (CHNS/O analyzer). To a stirred solution of 0.6 g [bmim]PF₆ in 25 cm³ methanol, 0.25 g CuCl₂·2H₂O (1.45 mmol) was added, then 1.0 g polystyrene-TEMPO resin. The mixture was stirred for 4 h at room temperature, then the solvent was evaporated under reduced pressure for 3 h to give a light red bead denoted PS-TEMPO@Cu-IL. Before use, the product was dried overnight at 50 °C under vacuum.

Typical experimental procedure for oxidation of alcohols

Alcohol (1.0 mmol) and 100 mg PS-TEMPO@Cu-IL were mixed with 5 cm³ *n*-octane and stirred at 65 °C under O₂ (1 atm) for the given time. After completion (monitored by TLC or GC), the catalyst can be easily collected by filtration. The recovered catalyst was used directly for the next run after simply washing with *n*-octane. The combined solvent phase was concentrated under vacuum. The crude product was purified by column chromatography (10:1 petroleum ether-ethyl acetate) to provide the analytically pure aldehyde. All products were known compounds and were characterized by ¹H NMR and IR spectroscopy; results were identical with data reported in the literature [36, 37].

Acknowledgments The authors are grateful for the support from the National Natural Science Foundation of China (50873042, 21001048), the Natural Science Fund of Jiangsu Province (BK2011399), the Key University Science Research Project of Jiangsu Province (11KJA430008), and the Jiangsu Marine Resource Development Research Institute Foundation (JSIMR10D03).

References

- Tojo G, Fernández M (2006) Oxidation of alcohols to aldehydes and ketones: a guide to current common practice. Springer, New York
- Wang XR, Yang HM, Feng B, Hou ZS, Hu Y, Qiao YX, Li H, Zhao XG (2009) Catal Lett 132:34
- Wang H, Deng S-X, Shen Z-R, Wang J-G, Ding D-T, Chen T-H (2009) Green Chem 11:1499
- Bawaked S, He Q, Dummer NF, Carley AF, Knight DW, Bethell D, Kiely CJ, Hutchings GJ (2011) Catal Sci Technol 1:747
- Choudhary VR, Dumbre DK (2009) Catal Commun 10:1738
- Enache DI, Knight DW, Hutchings GJ (2005) Catal Lett 103:43
- Choudhary VR, Dumbre DK, Narkhede VS, Jana SK (2003) Catal Lett 86:229
- Yu H, Zhang Y, Fu XB, Peng F, Wang HJ, Yang J (2009) Catal Commun 10:1752
- Hosokawa S, Hayashi Y, Imamura S, Wada K, Inoue M (2009) Catal Lett 129:394
- Liu L, Ma J, Xia J, Li L, Li C, Zhang X, Gong J, Tong Z (2011) Catal Commun 12:323
- Geisslmeier D, Jary WG, Falk H (2005) Monatsh Chem 136:1591
- Hanson SK, Wu RL, Silks LA (2011) Org Lett 13:1908
- Chen YT, Chen W, Tang QH, Guo Z, Yang YH, Su FB (2011) Catal Lett 141:149
- Karimi B, Farhangi E (2011) Chem Eur J 17:6056
- Bolm C, Fey T (1999) Chem Commun 1795
- Karimi B, Badreh E (2011) Org Biomol Chem 9:4194
- Matsumoto K, Iwata T, Suenaga M, Okudomi M, Nogawa M, Nakano M, Sugahara A, Bannai Y, Baba K (2010) Heterocycles 81:2539
- Pozzi G, Cavazzini M, Quici S, Benaglia M, Dell'Anna G (2004) Org Lett 6:441
- Weik S, Nicholson G, Jung G, Rademann J (2001) Angew Chem Int Ed 40:1436
- Brunel D, Fajula F, Nagy JB, Deroide B, Verhoef MJ, Veum L, Peters JA, van Bekkum H (2001) Appl Catal A Gen 213:73
- Dijksman A, Arends I, Sheldon RA (2001) Synlett 102
- Tundo P, Perosa A (2007) Chem Soc Rev 36:532
- Gu YL, Li GX (2009) Adv Synth Catal 351:817
- Collis AEC, Horvath IT (2011) Catal Sci Technol 1:912
- Gu Y, Ogawa C, Kobayashi J, Mori Y, Kobayashi S (2006) Angew Chem Int Edit 45:7217
- Kernchen U, Etzold B, Korth W, Jess A (2007) Chem Eng Technol 30:985
- Arras J, Steffan M, Shayeghi Y, Ruppert D, Claus P (2009) Green Chem 11:716
- Moucel R, Perrigaud K, Goupil JM, Madec PJ, Marinel S, Guibal E, Gaumont AC, Dez I (2010) Adv Synth Catal 352:433
- Sobota M, Happel M, Amende M, Paape N, Wasserscheid P, Laurin M, Libuda J (2011) Adv Mater 23:2617
- Rodriguez-Perez L, Pradel C, Serp P, Gomez M, Teuma E (2011) ChemCatChem 3:749
- Liu L, Ji LY, Wei YY (2008) Catal Commun 9:1379
- Liu L, Ji L-Y, Wei Y-Y (2008) Monatsh Chem 139:901
- Liu L, Ma JJ, Ji LY, Wei YY (2008) J Mol Catal A Chem 291:1
- Yue C, Fang D, Liu L, Yi T-F (2011) J Mol Liq 163:99
- Liu L, Ma JJ, Sun Z, Zhang JP, Huang JJ, Li SZ, Tong ZW (2011) Can J Chem 89:68
- Pouchert CJ (1985) The Aldrich library of FT-IR spectra. Aldrich Chemical Co, Milwaukee
- Pouchert CJ (1993) The Aldrich library of ¹³C and ¹H FT-NMR spectra. Aldrich Chemical Co, Milwaukee