Catalysis Communications 67 (2015) 90–94

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Asymmetric transfer hydrogenation of ketones catalyzed by thermoregulated ionic liquid-regulating ruthenium complexes

Xuerui Liu, Chen Chen, Yuhe Xiu, Angjun Chen, Li Guo, Ran Zhang, Jizhong Chen, Zhenshan Hou *

Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai, 200237, China

ARTICLE INFO

Article history:
Received 5 February 2015
Received in revised form 8 April 2015
Accepted 9 April 2015
Available online 11 April 2015

Keywords:
Asymmetric transfer hydrogenation
Ionic liquid
Thermoregulated phased-separation
Ruthenium complexes

ABSTRACT

A sulfonated chiral diamine ligand anion-based functionalized ionic liquid has been synthesized. Then the new ionic liquid-regulating ruthenium complexes were prepared successfully and employed as efficient catalysts for the asymmetric transfer hydrogenation of various ketones. The catalysts were highly efficient for the hydrogenation of a wide range of substrates bearing different functional groups and could be separated easily from the reaction mixture by thermoregulated phase separation, which can be efficiently recycled five times without significant changes in catalytic activity and enantioselectivity.

1. Introduction

Asymmetric transfer hydrogenation (ATH) has been widely used as an efficient and practical method for preparation of optically pure secondary alcohols that are important key intermediates for the synthesis of a large number of pharmaceutical substances [1]. Catalytic asymmetric hydrogenation is a powerful method for the synthesis of enantiomerically pure compounds [2]. The design of organometallic complexes containing chiral ligand is the fundamental importance for asymmetric catalysis. One of the most attractive catalytic system was developed by Noyori [3], which was based on Ru-TsDPEN (TsDPEN = N-(p-tolylsulfonyl)-1,2-diphenylethylenediamine) complex catalysts with the successful use of HCOOH-NEt_3 azeotropic mixture as hydrogen donor for asymmetric transfer hydrogenation of ketones. In many cases, high activity and enantioselectivity can be achieved with this archetypal catalyst [4].

Ruthenium [5,6] rhodium [7] and iridium [8] complexes using chiral phosphines or amines as ligands exhibited excellent performance in the asymmetric homogeneous hydrogenation of prochiral ketones and other carbonyl compounds. Although numerous highly efficient homogeneous asymmetric catalysts have been developed for ATH in the past decades, the drawback of homogeneous asymmetric catalysis is obvious, such as difficulty in separating product and recycling of the catalyst. To date, only a few recyclable homogeneous catalysts have been reported in the ATH of ketones. For example, they could be separated and recycled through organometal silylated [9], fluorous-tagged and clathrate-enabled technologies [10,11], but the preparation of these catalysts is very complicated. Therefore, a universal method for recovering homogeneous catalysts is still a challenge for the ATH of ketones.

The thermoregulated phase-separation system provided an alternative approach to recycle homogeneous catalysts. This system combines the advantage of homogeneous catalysis with excellent activity and heterogeneous catalysis with the simple method of biphasic catalyst/product separation [12,13]. In this aspect, the thermoregulated phase-separable phosphine ruthenium complex catalyst has been used in catalytic hydrogenation [14], as well as hydroformylation of diisobutylene [15]. Recently, the cooperative effect regulated by a thermoregulated ionic liquid has been suggested by our group in catalytic hydrogenation and epoxidation of olefins [16,17]. However, to the best of our knowledge, the thermoregulated phase-separable catalysts have never been applied to the ATH of ketones up to now.

Here we report on the synthesis of thermoregulated ionic liquid catalysts consisting of poly(ethylene glycol) functionalized imidazolium cations and ruthenium complex anions. The cations of the ionic liquid can regulate the thermoregulated property while the anions play a pivotal role in offering the catalytic active center for the ATH of ketones. From the viewpoint of green catalysis, more attention needs to be paid to the use of environmentally benign media. The current catalyst showed excellent performance for thermoregulated phase-separation in low toxic ethyl acetate media. In a word, we report a new temperature-dependent catalytic system, affording high catalytic activities and good enantioselectivities for the ATH of ketones with HCOOH-Et_3N azeotrope as the hydrogen donor.

---

* Corresponding author.
E-mail address: houzhenshan@ecust.edu.cn (Z. Hou).

http://dx.doi.org/10.1016/j.catcom.2015.04.013
1566-7367/

2. Experimental section

The PEG chain-functionalized N-dodecylimidazolium dichlorides ([PEG-4000-C_8MIM] Cl_2) [18] and sulfonated N-(p-tolylsulfonyl)-1,2-diphenylethylenediamine (TsDPENDS, sodium salt) were prepared according to the previously reported procedure [19], and then the ionic liquid [PEG-4000-C_8MIM][TsDPENDS] was prepared conveniently by anion exchange in CH_2Cl_2. Thus the ionic liquid-regulating ruthenium complex [PEG-4000-C_8MIM][Ru-TsDPENDS] was obtained according to Scheme 1. The other catalysts [PEG-m-C_nMIM][Ru-TsDPENDS] were synthesized in a similar manner, where m represented the molecular weight of PEG and n alkyl chain length was tethered in imidazolium ring. All synthetic procedures and characterization of the ionic liquid-regulating ruthenium complexes have been afforded in the supporting information (Figs. 1S–15S).

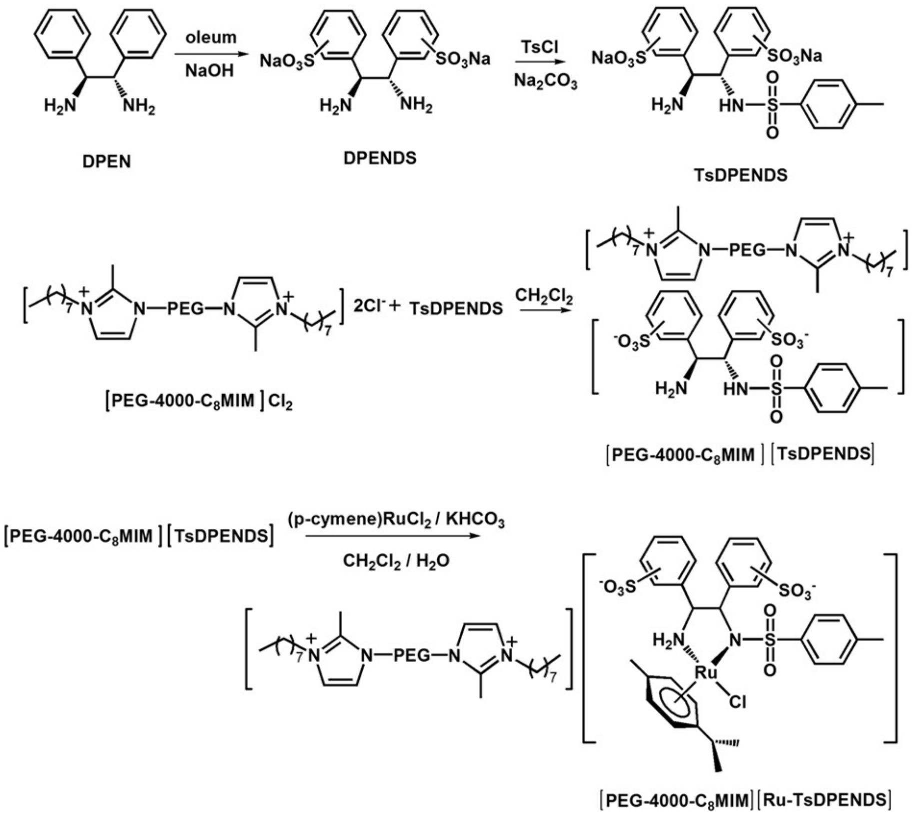
3. Results and discussion

3.1. Catalyst characterization

The ionic liquid-regulating ruthenium catalysts [PEG-m-C_nMIM][Ru-TsDPENDS] were characterized by ^{1}H NMR spectroscopy, ESI-MS, and elemental analysis (supporting information). The ^{1}H NMR spectra confirmed the formation of the proposed ruthenium arene complexes with sulfonated diamine ligand. In anion moiety, all proton resonances of the ethylenediamine, p-cymene and methyl groups of the isopropyl group were non-equivalent. The ESI-MS data of the catalysts were in agreement with the proposed structures and showed one group of peaks at 378.99 values corresponding to the molecular anion $\{[\text{Ru-TsDPENDS}]\text{-HCl}\}^{2-}$ (Figs. 3S, 5S and 7S). The results of ^{1}H NMR spectroscopy and ESI-MS on $\{(\text{p-cymene})\text{RuCl}_2\}_2$ part were similar to those of previously reported ruthenium complexes for the ATH of ketones in water [20]. In addition, the UV/vis spectra of [PEG-4000-C_8MIM][TsDPENDS], $\{(\text{p-cymene})\ \text{RuCl}_2\}_2$ and [PEG-4000-C_8MIM][Ru-TsDPENDS] have been performed. As shown in Fig. 1a, the absorbance at 260–270 nm can be assigned to adsorption of imidazolium and aromatic rings in [PEG-4000-C_8MIM][TsDPENDS] (Fig. 1a). However, a peak at 410 nm was attributed to Cl p → Ru d transition (Fig. 1b), and it was moved to 565 nm after the diamine ligand was coordinated with Ru as shown in (Fig. 1c). The shift of adsorbing wavelength demonstrated that diamine ligand was coordinated with Ru complex. The similar shift was also found in the UV/vis spectra of [PEG-4000-C_4MIM][Ru-TsDPENDS] and [PEG-4000-C_1MIM][Ru-TsDPENDS] (Figs. 8S and 9S). Actually, the phenomenon has been observed in molecularly imprinted Ru-complex catalysts for the ATH in water media [21]. On the basis of the results of elemental analysis of C, H, N and ICP-AES analysis of Ru, the ionic liquid catalysts [PEG-m-C_nMIM][Ru-TsDPENDS] have been synthesized successfully. The thermal stability of the ionic liquid catalyst was examined by using the TGA method (Fig. 10S). The onset decomposing temperature was around 250 °C and almost decomposed completely at 600 °C.

3.2. Catalytic performance

From our previous work, it was known that poly(ethylene glycol)-2000 functionalized 1-alkylate-2-methylimidazolium chloride ([PEG-2000-C_{12}MIM]Cl_2), coupled with EtOAc as the solvent, exhibits a strong thermoregulated behavior [16]. Thus, in this work we first prepared poly(ethylene glycol) functionalized imidazolium chloride. To obtain high enantioselectivity, the mono-N-tosylated derivative TsDPENDS was chosen as anion of the ionic liquid. Therefore, the as-obtained ionic liquid was composed of poly(ethylene glycol)-functionalized alkylimidazolium cation and TsDPENDS anion. The cation of ionic liquid provided the thermoregulated property while the anion played a pivotal role in providing a chiral center for Ru coordination.



Scheme 1. Typical procedure for preparing the ionic liquid catalyst [PEG-4000-C_8MIM] [Ru-TsDPENDS].