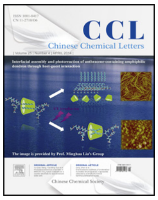
Chinese Chemical Letters 25 (2014) 613–616

Contents lists available at ScienceDirect

Chinese Chemical Letters

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



Original article

Immobilization of chiral Rh catalyst on glass and application to asymmetric transfer hydrogenation of aryl ketones in aqueous media

Tan-Yu Cheng *, Jing-Lan Zhuang, Hui Yao, Huai-Sheng Zhang, Guo-Hua Liu *

Key Laboratory of Resource Chemistry of Ministry of Education, College of Life and Environmental Science, Shanghai Normal University, Shanghai 200234, China

ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form 10 December 2013
Accepted 24 December 2013
Available online 10 January 2014

Keywords:
Heterogeneous Rh catalyst
Asymmetric transfer hydrogenation
Aromatic ketones
Glass substrate

ABSTRACT

A chiral catalyst, Cp*RhTsDPEN (Cp* = pentamethyl cyclopentadiene, TsDPEN = substitutive phenylsulfonyl-1,2-diphenylethylenediamine), was synthesized and immobilized at the surface of glass. The immobilized catalyst exhibited good catalytic efficiency for asymmetric transfer hydrogenation of aromatic ketones in water with HCOONa as hydrogen source.

1. Introduction

Self-assembled monolayers (SAMs) are an excellent tool to change surface properties of materials. The method has attracted a lot of interest and has developed rapidly in the past years. Nanotechnology has developed rapidly in recent decades, and it is widely used in several areas. SAMs are often used to prepare nanoparticles [1–3], because most nanoparticles need to be functionalized and have their biological toxicity reduced. Glass plates are also good supports for functional molecules. Fluorescent sensors were assembled on glass, which were used for the detection of nitroaromatic compounds in the vapor phase [4–6]. Fluorescent proteins were immobilized on glass surfaces, and they were very important for potential applications in bionanotechnology [7]. Some metal catalysts were supported on glass surfaces, which were used to catalyze oxidation reactions [8,9].

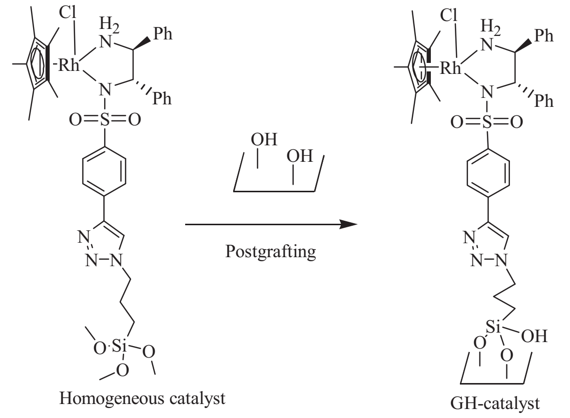
Chiral compounds are very important in our daily life, especially in medicinal chemistry, because different configurations have different drug activities. As such, enantioselective synthesis has attracted increasing interest from chemists during the past few decades. There are three main approaches to asymmetric synthesis, which are chiral pool synthesis, chiral auxiliaries, and asymmetric catalysis. Asymmetric transfer hydrogenation (ATH) is one of the most important asymmetric catalytic reactions, and it is normally promoted by transition metal catalysts [10–17]. Noyori *et al.* found that chiral TsDPEN exhibited excellent catalytic activity and enantioselectivity in the asymmetric transfer hydrogenation of aromatic ketones [18], and they have made outstanding contributions in this area [19,20]. Compared with homogeneous catalysts, heterogeneous immobilization molecular catalysts at the surfaces of materials have several outstanding advantages, including facile product purification, easy catalyst recovery from reaction mixtures and reusability. Normally, the materials used for immobilizing molecular catalysts are mesoporous silica [21,22], magnetic materials [23], zeolites [24], organic polymers [25], or high surface area carbon [26]. However, to the best of our knowledge there is no chiral catalyst that is immobilized on a glass surface.

What we are interested in is material supported catalysts in an effort to achieve highly active and recyclable heterogeneous catalysts [27–31]. Herein, the ligand of TsDPEN (substitutive phenylsulfonyl-1, 2-diphenylethylenediamine) with ethynyl group was synthesized, and the ligand was conjuncted with a silica source *via* click chemistry. Then, the homogeneous catalyst was prepared through stirring the solution of the ligand and $[Cp^*RhCl_2]_2$ in dichloromethane at room temperature. At last, the obtained catalyst was immobilized at the surface of glass plates to form the heterogeneous catalyst, which showed good catalytic efficiency and enantioselectivity.

---

* Corresponding authors.
E-mail addresses: tycheng@shnu.edu.cn (T.-Y. Cheng), ghliu@shnu.edu.cn (G.-H. Liu).

http://dx.doi.org/10.1016/j.cclet.2014.01.007



Scheme 1. Preparation of heterogeneous catalyst supported on glass.

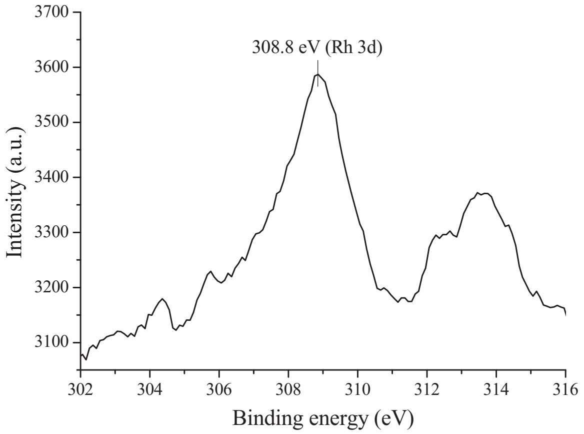


Fig. 1. XPS spectrum of the Rh active site within GH-catalyst.

2. Experimental

2.1. Preparation of the glass containing hydroxyl group

Microscope glass slides were used for monolayer preparation. The substrates were oxidized with piranha solution for 15 min (concentrated H_2SO_4 and 33% aqueous H_2O_2 in 3:1 ratio; caution: piranha should be handled carefully) and rinsed with MilliQ water (MQ). After drying with nitrogen stream, the substrates were used immediately to provide a freshly hydroxyl terminated surface on which to form the silanized monolayer.

2.2. Preparation of glass-supported heterogeneous catalyst (GH-catalyst)

As shown in Scheme 1, processed glass were immersed in the solution of silanizing homogeneous catalyst in CH_2Cl_2 until the solvent evaporated completely. To remove the unreacted homogeneous catalyst, the prepared glass were treated with ultrasound in CH_2Cl_2 and EtOH. The glass-supported heterogeneous catalyst (GH-catalyst) was obtained after the glass dried.

2.3. Typical catalytic procedure

A typical procedure was as follows [32]: GH-catalyst, HCOONa (20 mg, 0.3 mmol), ketones (2.0 mmol), and 2.0 mL water were added in a 10 mL round bottom flask. The mixture was allowed to react at 40 °C for 4 h. During the reaction, it was monitored constantly by TLC. The conversion and *ee* value could be determined by chiral GC using a Supelco β-Dex 120 chiral column (30 m × 0.25 mm (i.d.), 0.25 μm film) or HPLC analysis with UV–vis detector using Daicel OJ-H chiral column (∅ 0.46 cm × 25 cm).

3. Results and discussion

3.1. XPS analysis of GH-catalyst

The click reaction was used for the synthesis of the TsDPEN ligand with the trimethoxysilane group, which combined with Rh to form the homogeneous catalyst (see Supporting information). The heterogeneous catalyst was synthesized by grafting the homogeneous catalyst onto the oxidized glass with excess hydroxy groups. According to the XPS data, the O/Si ratio of normal glass was 1.53, and that of oxidized glass was 2.11. That indicated that excess hydroxy groups were obtained after the glass was oxidized. The content of sulfur increased from 0 to 0.61%. This was because a few sulfonic groups were produced when the glass was oxidized by sulfuric acid. The glass we used were normal slides, so there was plentiful carbon according to the XPS data. After grafting the homogeneous catalyst onto the slides, the XPS N1s and Rh3d signals indicated that the catalyst was immobilized successfully. As shown in Fig. 1, the binding energy of Rh3d was 308.8 eV, which was nearly the same with Cp*RhTsDPEN (309.3 eV).

3.2. AFM analysis of GH-catalyst

The resulting AFM images are shown in Fig. 2. The surface roughness exhibited by the root-mean-square (RMS) height value for glass was 2.60 nm. After grafting, the RMS value for the catalyst 6 decreased to 2.19 nm. This decrease in roughness can be

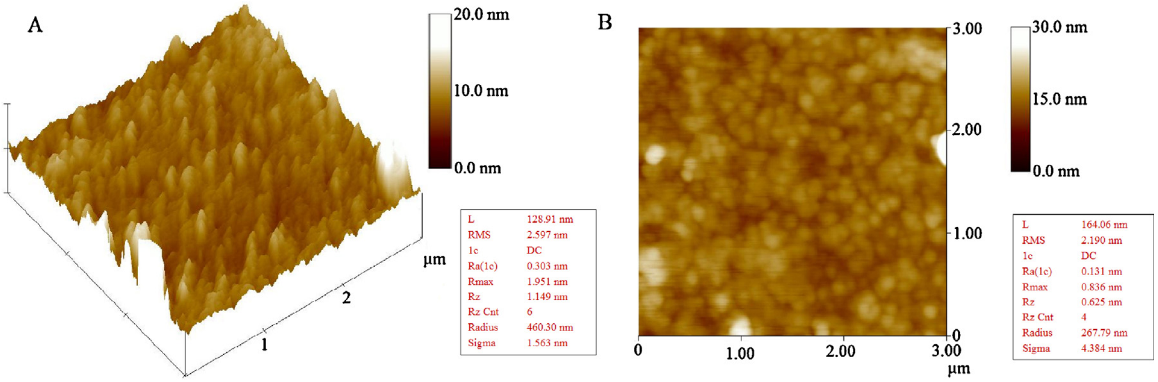
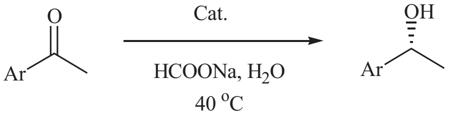


Fig. 2. AFM images of the glass (A) and GH-catalyst (B).

Table 1
Asymmetric transfer hydrogenation of aromatic ketones.[a]



Entry	Ar	Conv.[b] (%)	*ee* (%)[b]
1	Ph	95	94
2	4-FPh	98	87
3	4-ClPh	93	91
4	4-BrPh	97	93
5	4-MePh	86	90
6	4-MeOPh	87	93
7	4-NO_2Ph	99	84
8	4-CF_3Ph	99	84
9	4-CNPh	84	85
10	3-MeOPh	94	93
11	3-Br	99	94
12	α-Acetonaphthone	85	80

[a] Reactions were carried out in water. Reaction conditions: catalysts (0.33 μmol of Rh, based on the ICP analysis), HCO_2Na (130 mg, 1.67 mmol), ketone (0.2 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (4 h) except 12 (for 6 h).

[b] Determined by chiral GC or HPLC analysis (see Supporting information).

explained by the grafted homogeneous catalyst decreasing the altitude difference.

3.3. *Catalytic performances of GH-catalyst for asymmetric transfer hydrogenation*

The catalytic activity of GH-catalyst was evaluated following successful preparation of heterogeneous catalyst. Table 1 summarizes catalytic performances for asymmetric transfer hydrogenation of aromatic ketones in aqueous medium. GH-catalyst delivered high conversions for most of the aromatic ketones and in most cases the enantioselectivities were good, with *ee* values reaching up to 93%. Comparing entries 2, 7, and 8 with 6 and 10, it was obvious that aromatic ketones with electron-drawing groups were generally more active than those with electron-donating groups. That may be because the electron-donating groups give lower LUMO values, which accelerates the catalytic reaction. Another advantage of GH-catalyst was the active centers were at the surface of the slides, which can show good catalytic activity for the huge size substrate (entry 12). In addition, the recyclability of GH-catalyst was also investigated with acetophenone as a substrate in the same conditions. GH-catalyst was recovered very easily and could be reused directly. However, the conversion at the third cycle was 25%, and decreased rapidly from 99% (the second cycle). That may because the active center was lost from the glass.

4. Conclusion

In conclusion, we have synthesized trimethoxysilane-substitute Cp*RhTsDPEN *via* click reaction that can be directly grafted onto oxidized glass slides to prepare heterogeneous catalysts. Using XPS and AFM, we have demonstrated the heterogeneous catalyst was prepared successfully. The catalyst displayed good catalytic activity and enantioselectivity in the asymmetric transfer hydrogenation of aromatic ketones in aqueous medium, and the substrates with electron-donating groups had more enantioselectivity than those with electron-drawing groups.

Acknowledgments

We are grateful to the Shanghai Sciences and Technologies Development Fund (Nos. 13ZR1458700 and 12nm0500500), the Shanghai Municipal Education Commission (Nos. 14YZ074, 12ZZ135), Shanghai Normal University (Nos. DXL122, SK201329) for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2014.01.007.

References

[1] R. Hong, G. Han, J.M. Fernández, et al., Glutathione-mediated delivery and release using monolayer protected nanoparticle carriers, J. Am. Chem. Soc. 128 (2006) 1078–1079.
[2] P.D. Jadzinsky, G. Calero, C.J. Ackerson, D.A. Bushnell, R.D. Kornberg, Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution, Science 318 (2007) 430–433.
[3] A. Verma, O. Uzun, Y. Hu, et al., Surface-structure-regulated cell-membrane penetration by monolayer-protected nanoparticles, Nat. Mater. 7 (2008) 588–595.
[4] G. He, G. Zhang, F. Lu, Y. Fang, Fluorescent film sensor for vapor-phase nitroaromatic explosives via monolayer assembly of oligo(diphenylsilane) on glass plate surfaces, Chem. Mater. 21 (2009) 1494–1499.
[5] L. Ding, Y. Liu, Y. Cao, et al., A single fluorescent self-assembled monolayer film sensor with discriminatory power, J. Mater. Chem. 22 (2012) 11574–11582.
[6] S. Zhang, F. Lü, L. Gao, L. Ding, Y. Fang, Fluorescent sensors for nitroaromatic compounds based on monolayer assembly of polycyclic aromatics, Langmuir 23 (2006) 1584–1590.
[7] N.P. Reynolds, J.D. Tucker, P.A. Davison, et al., Site-specific immobilization and micrometer and nanometer scale photopatterning of yellow fluorescent protein on glass surfaces, J. Am. Chem. Soc. 131 (2009) 896–897.
[8] S. Nakagaki, A.R. Ramos, F.L. Benedito, P.G. Peralta-Zamora, A.J.G. Zarbin, Immobilization of iron porphyrins into porous vycor glass: characterization and study of catalytic activity, J. Mol. Catal. A: Chem. 185 (2002) 203–210.
[9] I.O. Benítez, B. Bujoli, L.J. Camus, et al., Monolayers as models for supported catalysts: zirconium phosphonate films containing manganese(III) porphyrins, J. Am. Chem. Soc. 124 (2002) 4363–4370.
[10] X. Wu, C. Wang, J. Xiao, Asymmetric transfer hydrogenation in water with platinum group metal catalysts, Platinum Met. Rev. 54 (2010) 3–19.
[11] R. Malacea, R. Poli, E. Manoury, Asymmetric hydrosilylation, transfer hydrogenation and hydrogenation of ketones catalyzed by iridium complexes, Coordin. Chem. Rev. 254 (2010) 729–752.
[12] T. Jerphagnon, R. Haak, F. Berthiol, et al., Ruthenacycles and iridacycles as catalysts for asymmetric transfer hydrogenation and racemisation, Top. Catal. 53 (2010) 1002–1008.
[13] C. Wang, X. Wu, J. Xiao, Broader, greener, and more efficient: recent advances in asymmetric transfer hydrogenation, Chem. Asian J. 3 (2008) 1750–1770.
[14] T. Ikariya, A.J. Blacker, Asymmetric transfer hydrogenation of ketones with bifunctional transition metal-based molecular catalysts, Acc. Chem. Res. 40 (2007) 1300–1308.
[15] S. Gladiali, E. Alberico, Asymmetric transfer hydrogenation: chiral ligands and applications, Chem. Soc. Rev. 35 (2006) 226–236.
[16] C. Bianchini, P. Barbaro, Recent aspects of asymmetric catalysis by immobilized chiral metal catalysts, Top. Catal. 19 (2002) 17–32.
[17] G. Zassinovich, G. Mestroni, S. Gladiali, Asymmetric hydrogen transfer reactions promoted by homogeneous transition metal catalysts, Chem. Rev. 92 (1992) 1051–1069.
[18] S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, Asymmetric transfer hydrogenation of aromatic ketones catalyzed by chiral ruthenium(II) complexes, J. Am. Chem. Soc. 117 (1995) 7562–7563.
[19] R. Noyori, S. Hashiguchi, Asymmetric transfer hydrogenation catalyzed by chiral ruthenium complexes, Acc. Chem. Res. 30 (1997) 97–102.
[20] R. Noyori, Asymmetric catalysis: science and opportunities (Nobel Lecture), Angew. Chem. Int. Ed. 41 (2002) 2008–2022.
[21] S. Minakata, M. Komatsu, Organic reactions on silica in water, Chem. Rev. 109 (2008) 711–724.
[22] C. Li, Chiral synthesis on catalysts immobilized in microporous and mesoporous materials, Catal. Rev. 46 (2004) 419–492.
[23] S. Shylesh, V. Schünemann, W.R. Thiel, Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis, Angew. Chem. Int. Ed. 49 (2010) 3428–3459.
[24] T. Maschmeyer, F. Rey, G. Sankar, J.M. Thomas, Heterogeneous catalysts obtained by grafting metallocene complexes onto mesoporous silica, Nature 378 (1995) 159–162.
[25] J. Lu, P.H. Toy, Organic polymer supports for synthesis and for reagent and catalyst immobilization, Chem. Rev. 109 (2009) 815–838.
[26] S.C. Petrosius, R.S. Drago, V. Young, G.C. Grunewald, Low-temperature decomposition of some halogenated hydrocarbons using metal oxide/porous carbon catalysts, J. Am. Chem. Soc. 115 (1993) 6131–6137.
[27] H. Zhang, R. Jin, H. Yao, et al., Core-shell structured mesoporous silica: a new immobilized strategy for rhodium catalyzed asymmetric transfer hydrogenation, Chem. Commun. 48 (2012) 7874–7876.

[28] Y. Sun, G. Liu, H. Gu, et al., Magnetically recoverable SiO_2-coated Fe_3O_4 nanoparticles: a new platform for asymmetric transfer hydrogenation of aromatic ketones in aqueous medium, Chem. Commun. 47 (2011) 2583–2585.

[29] G. Liu, H. Gu, Y. Sun, et al., Magnetically recoverable nanoparticles: highly efficient catalysts for asymmetric transfer hydrogenation of aromatic ketones in aqueous medium, Adv. Synth. Catal. 353 (2011) 1317–1324.

[30] G. Liu, J. Wang, T. Huang, et al., Mesoporous silica-supported iridium catalysts for asymmetric hydrogenation reactions, J. Mater. Chem. 20 (2010) 1970–1975.

[31] G. Liu, Y. Sun, J. Wang, et al., Microwave-assisted tandem allylation-isomerization reaction catalyzed by a mesostructured bifunctional catalyst in aqueous media, Green Chem. 11 (2009) 1477–1481.

[32] X. Wu, X. Li, A. Zanotti-Gerosa, et al., RhIII- and IrIII-catalyzed asymmetric transfer hydrogenation of ketones in water, Chem. Eur. J. 14 (2008) 2209–2222.